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Organic Chemical Manufacturing. Volume 8
Selected Processes

IT Enviroscience
Knoxville, TN

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EPA is developing new source performance standards under Section 111 of the Clean Air Act and national emission standards for hazardous air pollutants under Section 112 for volatile organic compound emissions (VOC) from organic chemical manufacturing facilities. In support of this effort, data were gathered on chemical processing routes, VOC emissions, control techniques, control costs, and environmental impacts resulting from control. These data have been analyzed and assimilated into the ten volumes comprising this report.

This volume presents in-depth studies of several major organic chemical products.

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Volume 8: Selected Processes

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

02

December 1980

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INTRODUCTION

A. SOCMI PROGRAM

Concern over widespread violation of the national ambient air quality standard for ozone (formerly photochemical oxidants) and over the presence of a number of toxic and potentially toxic chemicals in the atmosphere led the Environmental Protection Agency to initiate standards development programs for the control of volatile organic compound (VOC) emissions. The program goals were to reduce emissions through three mechanisms: (1) publication of Control Techniques Guidelines to be used by state and local air pollution control agencies in developing and revising regulations for existing sources; (2) promulgation of New Source Performance Standards according to Section 111(b) of the Clean Air Act; and (3) promulgation, as appropriate, of National Emission Standards for Hazardous Air Pollutants under Section 112 of the Clean Air Act. Most of the effort was to center on the development of New Source Performance Standards.

One program in particular focused on the synthetic organic chemical manufacturing industry (SOCMI), that is, the industry consisting of those facilities primarily producing basic and intermediate organics from petroleum feedstock meterials. The potentially broad program scope was reduced by concentrating on the production of the nearly 400 higher volume, higher volatility chemicals estimated to account for a great majority of overall industry emissions. EPA anticipated developing generic regulations, applicable across chemical and process lines, since it would be practically impossible to develop separate regulations for 400 chemicals within a reasonable time frame.

To handle the considerable task of gathering, assembling, and analyzing data to support standards for this diverse and complex industry, EPA solicited the technical assistance of IT Enviroscience, Inc., of Knoxville, Tennessee (EPA Contract No. 68-02-2577). IT Enviroscience was asked to investigate emissions and emission controls for a wide range of important organic chemicals. Their efforts focused on the four major chemical plant emission areas: process vents, storage tanks, fugitive sources, and secondary sources (i.e., liquid, solid, and aqueous waste treatment facilities that can emit VOC).

B. REPORTS

To develop reasonable support for regulations, IT Enviroscience gathered data on about 150 major chemicals and studied in-depth the manufacture of about 40 chemical products and product families. These chemicals were chosen considering their total VOC emissions from production, the potential toxicity of emissions, and to encompass the significant unit processes and operations used by the industry. From the in-depth studies and related investigations, IT Enviroscience prepared 53 individual reports that were assembled into 10 volumes. These ten volumes are listed below:

Volume I : Study Summary
Volume II : Process Sources
Volume III : Storage, Fugitive, and Secondary Sources
Volume IV : Combustion Control Devices
Volume V : Adsorption, Condensation, and Absorption Devices
Volume VI-X: Selected Processes

This volume is a compilation of individual reports for the following chemical products: ethylene dichloride, carbon tetrachloride, perchloroethylene, fluorocarbons, 1,1,1-trichloroethane, trichloroethylene, vinylidene, and chloromethanes. The reports generally describe processes used to make the products, VOC emissions from the processes, available emission controls, and the costs and impacts of those controls (except that abbreviated reports do not contain control costs and impacts). Information is included on all four emission areas; however, the emphasis is on process vents. Storage tanks, fugitive sources, and secondary sources are covered in greater detail in Volume III. The focus of the reports is on control of new sources rather than on existing sources in keeping with the main program objective of developing new source performance standards for the industry. The reports do not outline regulations and are not intended for that purpose, but they do provide a data base for regulation development by EPA.

C. MODEL PLANTS

To facilitate emission control analyses, the reports introduce the concept of a "model plant" (not in abbreviated reports). A model plant by definition is a
06 representation of a typical modern process for production of a particular chemical. Because of multiple production routes or wide ranges in typical production

capacities, several model plants may be presented in one product report. The model plants can be used to predict emission characteristics of a new plant. Of course, describing exactly what a new plant will be like is difficult because variations of established production routes are often practiced by individual companies. Nonetheless, model plants provide bases for making new-plant emission estimates (uncontrolled and controlled), for selecting and sizing controls for new plants, and for estimating cost and environmental impacts. It is stressed that model-plant analyses are geared to new plants and therefore do not necessarily reflect existing plant situations.

REPORT 1

ETHYLENE DICHLORIDE

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Prepared for
Emission Standards and Engineering Division
Office of Air Quality Planning and Standards
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Research Triangle Park, North Carolina

October 1980

This report contains certain information which has been extracted from the Chemical Economics Handbook, Stanford Research Institute. Wherever used, it has been so noted. The proprietary data rights which reside with Stanford Research Institute must be recognized with any use of this material.

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870 X 10^{-6}
Joule (J)	British thermal unit (Btu)	9.480 X 10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531 X 10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643 X 10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585 X 10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340 X 10^{-3}
Meter (m)	Inch (in.)	3.937 X 10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450 X 10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778 X 10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^{9}	1 Gg = 1 X 10^{9} grams
M	mega	10^{6}	1 Mg = 1 X 10^{6} grams
k	kilo	10^{3}	1 km = 1 X 10^{3} meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Ethylene dichloride (EDC) was selected for consideration because preliminary estimates indicated that the large amounts produced and the moderate to high volatility of the chemicals involved in its manufacture would result in high emissions of volatile organic compounds (VOC) (see Appendix A for pertinent physical properties). Ethylene dichloride also constitutes a large portion of the emissions from both direct chlorination and oxychlorination of ethylene, the two commercial processes for its manufacture.

B. USAGE AND GROWTH

The end uses and expected growth rates for ethylene dichloride are given in Table II-1. The predominant use is as an intermediate in the production of vinyl chloride monomer (VCM); approximately 96% of the VCM produced in 1979 was made from ethylene dichloride. A large portion of the remaining ethylene dichloride is used in production of chlorinated solvents.[1]

The domestic ethylene dichloride capacity for 1978 is reported to be about 6,920,000 Mg/yr.[2] Production was reported to be about 4,990,000 Mg in 1978,[3] or about 70% of capacity. Based on a projected growth rate of 5 to 6.5%,[1] production will utilize 92 to 100% of the 1978 capacity by 1982. Several companies are either completing construction and startup of new VCM plants or are planning new VCM capacity,[1,4] which usually must include additional ethylene dichloride capacity. Ethylene dichloride for sale must come from direct chlorination of ethylene unless a supply of hydrogen chloride (HCl) is available as feed for the oxychlorination process. Conversely, unless the HCl produced as a by-product during the cracking of ethylene dichloride to VCM has another use, it is used as feed for the oxychlorination process.[1]

C. DOMESTIC PRODUCERS

There were 12 producers operating 18 ethylene dichloride plants in the United States in 1979. Table II-2[1,2,4,5] lists the producers, locations, and capacities; Fig. II-1 shows plant locations.

Table II-1. Ethylene Dichloride Usage and Growth*

End Use	Production for 1978 (%)	Average Growth for 1977--1982 (%/yr)
Vinyl chloride	87	5.5 - 7.5
1,1,1-Trichloroethane	4	4.0 - 5.5
Trichloroethylene	2	(-2.0) - 3.5
Perchloroethylene	2	0 - 2.0
Ethyleneamines	2	(-2.5) - (-3.5)
Vinylidene chloride	2	5.0 - 7.0
Lead scavanger	1	(-15.0)

*See ref 1.

Table II-2. Ethylene Dichloride Capacity[a]

Plant	Location	Capacity as of 1979 (Mg/yr)
ICI	Baton Rouge, LA	315,000
Borden	Geismar, LA	225,000[b]
Conoco	Lake Charles, LA	524,000[c]
Diamond Shamrock	Deer Park, TX	145,000
Diamond Shamrock	La Porte, TX	719,000
Dow	Freeport, TX	726,000
Dow	Oyster Creek, TX	499,000
Dow	Plaquemine, LA	953,000
Ethyl	Baton Rouge, LA	318,000
Ethyl	Houston, TX	118,000
Goodrich	Calvert City, KY	454,000[d]
PPG	Lake Charles, LA	544,000
PPG	Guayanilla, PR	379,000[e]
Shell	Deer Park, TX	635,000
Shell	Norco, LA	544,000
Stauffer	Long Beach, CA	154,000
Union Carbide	Taft, LA	68,000[f]
Union Carbide	Texas City, TX	68,000[f]
Vulcan	Geismar, LA	136,000
Total		7,524,000[g]

[a] See refs 1,2,4 and 5.

[b] Plant started up in 1977 (see ref 5).

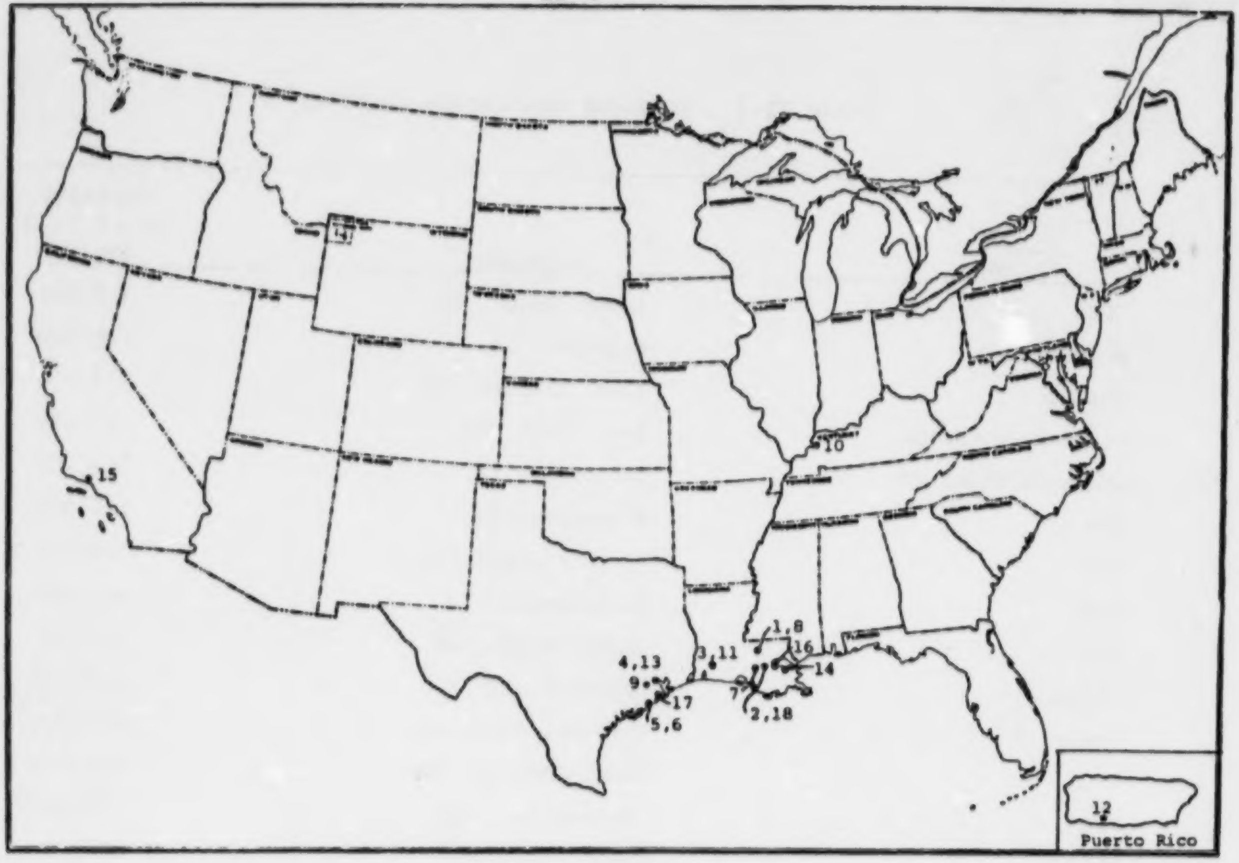
[c] Conoco plans to add 318,000 Mg/yr by 1982 (see ref 4).

[d] Convent Chemical, a joint venture of Goodrich and Bechtel, is building a 363,000-Mg/yr ethylene dichloride facility near Convent, LA (see ref 4).

[e] Plant is shut down.

[f] Union Carbide is the only producer making ethylene dichloride exclusively by the direct-chlorination of ethylene process; all other producers use both the direct-chlorination and the oxychlorination processes (see ref 1).

[g] Georgia-Pacific is building a 748,000 Mg/yr ethylene dichloride unit at Plaquemine, LA, and Formosa Plastics is building an ethylene dichloride unit with an estimated capacity of 385,000 Mg/yr at Point Comfort, TX.



(1) ICI Americas, Inc., Baton Rouge, LA
(2) Borden Chemical Co., Geismar, LA
(3) Conoco Chemicals, Lake Charles, LA
(4) Diamond Shamrock Corp., Deer Park, TX and La Porte, TX
(5) Dow Chemical Co., Freeport, TX
(6) Dow Chemical Co., Oyster Creek, TX
(7) Dow Chemical Co., Plaquemine, LA
(8) Ethyl Corp., Baton Rouge, LA
(9) Ethyl Corp., Houston, TX
(10) B.F. Goodrich Co., Calvert City, KY
(11) PPG Industries, Inc., Lake Charles, LA
(12) PPG Industries, Inc., Guayanilla, PR
(13) Shell Chemical Co., Deer Park, TX
(14) Shell Chemical Co., Norco, LA
(15) Stauffer Chemical Co., Long Beach, CA
(16) Union Carbide Corp., Taft, LA
(17) Union Carbide Corp., Texas City, TX
(18) Vulcan Materials Co., Geismar, LA

Fig. II-1. Locations of Plants Manufacturing Ethylene Dichloride

Companies producing EDC are listed below:

1. ICI

   About 70% of the EDC capacity is required to operate the VCM facilities at capacity. The remainder is sold.[1]

2. Borden

   All EDC is captively consumed in the manufacture of VCM. The facilities were started up in 1977.[5]

3. Conoco

   All EDC is captively consumed in the manufacture of VCM.[1] The plans are to add 318,000 Mg/yr to their capacity by 1982.[4]

4. Diamond Shamrock

   All EDC produced at LaPorte, TX, is consumed in the manufacture of VCM. Some of the EDC capacity at Deer Park, TX, is required for the perchloroethylene facilities; the rest of the EDC is sold.[1,6]

5. Dow

   Approximately 75% of the EDC capacity is used as an intermediate for capacity production of numerous end products; the remainder is sold.[1]

6. Ethyl

   Nearly all the EDC capacity is required as an intermediate for the manufacture of various end products.[1]

7. Goodrich

   All EDC is captively consumed in VCM production.[1] Goodrich and Bechtel have agreed on a joint venture to manufacture EDC at a facility near Houston, TX.[4]

8. PPG

   Nearly all EDC is captively consumed in the manufacture of VCM and other chlorinated hydrocarbons.[1]

9. Shell

EDC is captively consumed in VCM manufacture.[1]

10. Stauffer

About 95% of the EDC is consumed in VCM production; the remainder is sold.[7]

11. Union Carbide

Union Carbide is the only producer making all EDC exclusively by the direct-chlorination process. About 85% of the EDC capacity is required for operation of ethylenediamine plants at capacity.[1]

12. Vulcan

A small amount of EDC is consumed in the manufacture of perchloroethylene; most of it is sold.[1]

D. REFERENCES*

1. S. A. Cogswell, "Ethylene Dichloride," pp. 651.5031A--651.5033I in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (February 1979).

2. 1979 Directory of Chemical Producers, United States of America, SRI International, Menlo Park, CA, p 598 (1979).

3. "Manual of Current Indicators--Supplemental Data," p. 256 in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (August 1980).

4. "Chemical Profile on Ethylene Dichloride," Chemical Marketing Reporter 217(18), 9 (May 5, 1980).

5. J. A. Key, IT Enviroscience, Inc., Trip Report for Visit to Borden Chemicals, Geismar, Louisiana, March 2, 1978 (data on file at EPA, ESED, Research Triangle Park, NC).

6. William R. Taylor, Diamond Shamrock Corp., Cleveland, OH, letter dated Mar. 6, 1979, to EPA.

7. Thomas J. Sayers, Stauffer Chemical Co., Westport, CT, letter dated Feb. 23, 1975, to EPA.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTION

A. INTRODUCTION

Most of the ethylene dichloride (EDC) produced domestically is used in the production of vinyl chloride monomer (VCM). Three principal steps are involved in producing VCM: (1) the direct chlorination of ethylene to yield EDC, (2) which is then cracked to yield VCM plus hydrogen chloride (HCl), and (3) the use of HCl with oxygen, which may be in the form of air, to oxychlorinate ethylene to produce additional EDC plus water. These steps constitute the "balanced" process, so-called because all the HCl is recycled.

This report is concerned with only the direct-chlorination process and the two variations of the oxychlorination process for producing ethylene dichloride. Also, for the model plants discussed in Sect. IV the ratio of EDC produced by direct chlorination to EDC produced by oxychlorination is fixed because no net HCl is produced. In other plants, however, such as one in which HCl is available as a by-product from other processes, the ratio will be different. One ethylene dichloride producer uses only the direct-chlorination process. Previously, ethylene dichloride was produced as a by-product of ethylene oxide manufacture by the chlorohydrin process; however, the last domestic producer using that process converted to propylene oxide manufacture in 1970.[1]

B. DIRECT-CHLORINATION AND OXYCHLORINATION (AIR) PROCESSES

Ethylene dichloride is produced by direct chlorination of ethylene by the catalytic reaction

$$\underset{\text{(ethylene)}}{CH_2{=}CH_2} \quad + \quad \underset{\text{(chlorine)}}{Cl_2} \quad \longrightarrow \quad \underset{\text{(ethylene dichloride)}}{ClCH_2CH_2Cl}$$

Almost all commercial plants now use a ferric chloride catalyst in a liquid-phase process.

Ethylene dichloride is also produced by oxychlorination of ethylene with hydrogen chloride and air or oxygen by the following catalytic reaction:

$$\underset{\text{(ethylene)}}{2CH_2{=}CH_2} + \underset{\text{(oxygen)}}{O_2} + \underset{\substack{\text{(hydrogen}\\ \text{chloride)}}}{4HCl} \longrightarrow \underset{\substack{\text{(ethylene}\\ \text{dichloride)}}}{2ClCH_2CH_2Cl} + \underset{\text{(water)}}{2H_2O}$$

The catalyst is a mixture of copper chloride and other chlorides and the reaction is carried out in the vapor phase in either a fixed- or fluid-bed reactor.

The typical ethylene dichloride process shown in Fig. III-1 begins with ethylene (Stream 1) being fed by pipeline to both the oxychlorination reactor and the direct-chlorination reactor. In the oxychlorination reactor the ethylene is mixed with approximately stoichiometric proportions of anhydrous hydrogen chloride (Stream 2) and air (Stream 3) at pressures of 140--520 kPa and temperatures of 200--315°C. The conversion of ethylene to ethylene dichloride in the reactor is virtually complete. The reaction is exothermic, generating more than 230 kJ of heat per mole of ethylene dichloride produced, and requires efficient heat removal for adequate temperature control.[2]

The products of reaction from the oxychlorination reaction are quenched and cooled (Stream 4) and then go to a knockout drum. The condensed crude ethylene dichloride and water (Stream 5) separated by the knockout drum enter a decanter, where the crude ethylene dichloride is separated from the aqueous phase. The crude ethylene dichloride (Stream 6) goes to in-process storage, and the aqueous phase (Stream 7) is recycled to the quench step. Noncondensed material (Stream 8) from the knockout drum is fed to an absorber, where ethylene dichloride is recovered from the nitrogen and other inert gases, which are released to the atmosphere (Vent A). Absorbed ethylene dichloride and the absorbent (Stream 9) enter a stripper that removes ethylene dichloride overhead (Stream 10), which then goes to crude ethylene dichloride storage. The stripped absorbent (Stream 11) from the stripper is recycled to the absorber.

In the direct-chlorination step of the balanced process, ethylene (Stream 1) and a stoichiometric amount of chlorine (Stream 12) are reacted at a temperature of 38--49°C and at pressures of 69--138 kPa. This process produces 218 kJ/mole (of EDC) of heat that must be removed for proper temperature control.[2]

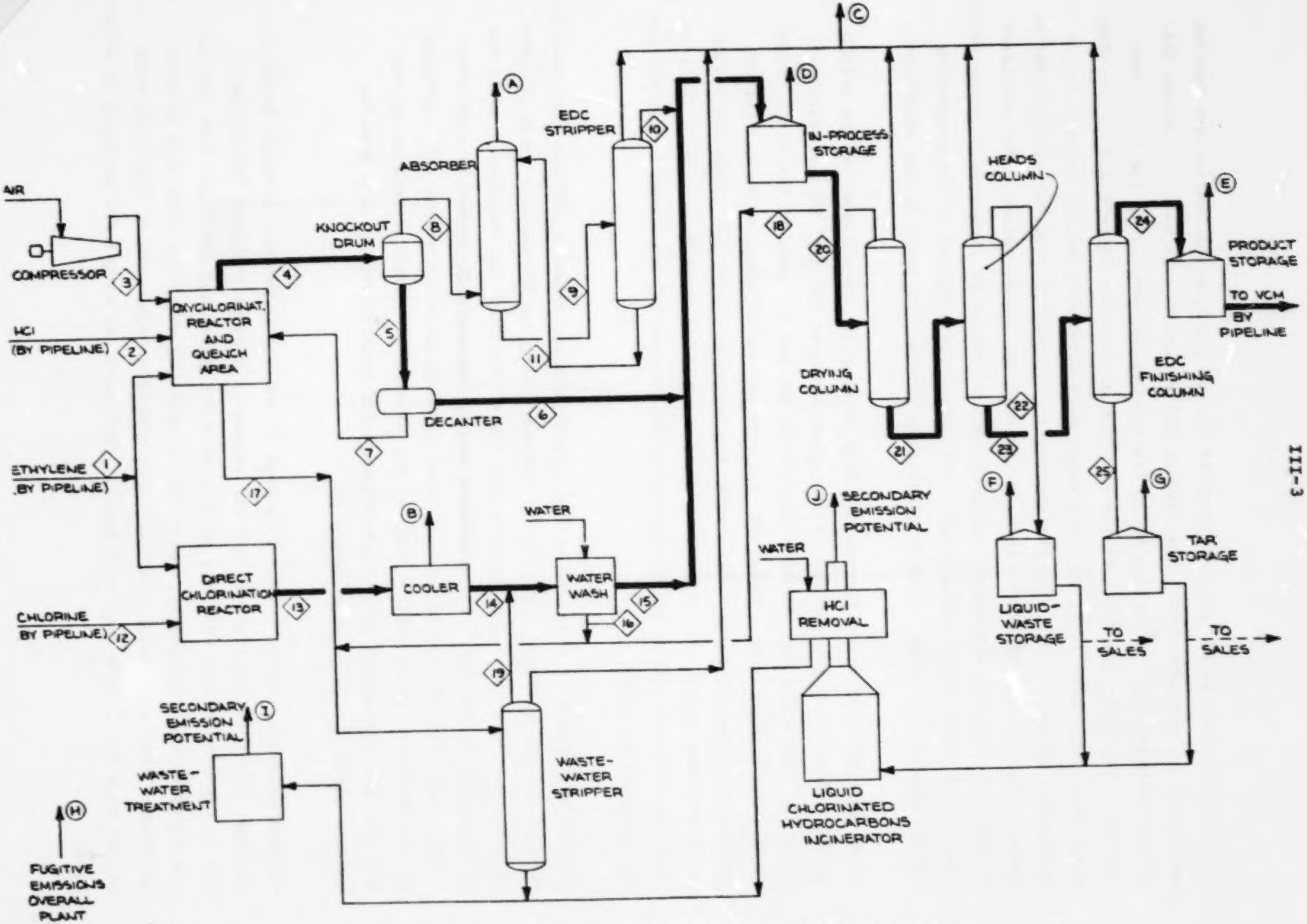
AIR
COMPRESSOR
3
HCl (BY PIPELINE)
2
ETHYLENE (BY PIPELINE)
1
CHLORINE (BY PIPELINE)
12
OXYCHLORINAT. REACTOR AND QUENCH AREA
DIRECT CHLORINATION REACTOR
4
KNOCKOUT DRUM
5
DECANTER
6
7
8
A
ABSORBER
EDC STRIPPER
9
10
11
13
17
B
COOLER
14
WATER
WATER WASH
15
16
19
WASTE-WATER STRIPPER
SECONDARY EMISSION POTENTIAL
I
WASTE-WATER TREATMENT
H
FUGITIVE EMISSIONS OVERALL PLANT
C
D
IN-PROCESS STORAGE
18
20
DRYING COLUMN
21
HEADS COLUMN
22
23
EDC FINISHING COLUMN
24
25
E
PRODUCT STORAGE
TO VCM BY PIPELINE
J
SECONDARY EMISSION POTENTIAL
WATER
HCl REMOVAL
LIQUID CHLORINATED HYDROCARBONS INCINERATOR
F
LIQUID-WASTE STORAGE
TO SALES
G
TAR STORAGE
TO SALES

Fig. III-1. Ethylene Dichloride from a Balanced Process

Products (Stream 13) of reaction from the direct-chlorination reactor are cooled, and the crude ethylene dichloride (Stream 14) is washed with water to remove dissolved hydrogen chloride before being transferred (Stream 15) to the in-process storage. Any inert gas fed with the ethylene or chlorine is released to the atmosphere from the cooler (Vent B). The waste wash water (Stream 16) is sent to the wastewater stripper along with the wastewater (Stream 17) from the oxychlorination quench area and the wastewater (Stream 18) from the drying column. The overheads (Stream 19) from the wastewater stripper, which consist of recovered ethylene dichloride, other chlorinated hydrocarbons, and water, are returned to the process by adding them to the crude ethylene dichloride (Stream 14) going to the water wash.

Crude ethylene dichloride (Stream 20) from in-process storage goes to the drying column, where water (Stream 18) is distilled overhead and sent to the wastewater stripper. The dry crude ethylene dichloride (Stream 21) goes to the heads column, which removes light ends (Stream 22) for storage and disposal or sale. Bottoms (Stream 23) from the heads column enter the ethylene dichloride finishing column, where ethylene dichloride (Stream 24) goes overhead to product storage. The tars from the ethylene dichloride finishing column (Stream 25) are taken to tar storage for disposal or sales.

The largest amount of emission is the oxychlorination reaction off-gas from vent A, because all the nitrogen from the air (Stream 3) fed to the reactor exits the process there. This vent also contains all the ethane from the ethylene feed to the oxychlorination reactor, carbon dioxide and carbon monoxide formed by side reactions, some ethylene dichloride and other chlorinated hydrocarbons not recovered by the absorber, and a small amount of the absorbent. Other process emissions are the vent gases from the direct-chlorination cooler (Vent B) and from the various distillation columns (Vents C).

Storage emission sources (Vents D through G) include in-process storage, product storage, liquid waste storage, and tar storage. Because ethylene dichloride is fed by pipeline to the cracking section of a VCM plant and the light ends and tars are piped to the incinerator, there are no handling emissions from this process as shown. They will occur, however, when ethylene dichloride or the light ends or the tars are loaded into tank trucks, tank cars, or barges for shipping to other sites.

Fugitive emissions (H) occur when leaks develop in valves or in pump or compressor seals. When the process pressures are higher than the cooling-water pressure, ethylene dichloride and other VOC can leak into the cooling water and escape as fugitive emissions from the cooling tower.

Secondary emissions can occur when wastewater containing VOC is sent to a wastewater treatment system or lagoon and the VOC are desorbed (I). Another source of secondary emissions is from the incineration of liquid-waste streams, where VOC are emitted with the flue gases (Vent J).

C. DIRECT-CHLORINATION AND OXYCHLORINATION (OXYGEN) PROCESSES

Only two domestic EDC producers use oxygen as the oxidant in the oxychlorination reactor. The process details are considered to be confidential by both producers. Although conceptual descriptions of such processes are given in the literature, it is not known how the processes actually used compare with those described. One producer has released data showing that the plant is not truly balanced; i.e., the ratio of ethylene dichloride from oxychlorination and direct chlorination differs from that of a balanced plant. However, both producers have direct chlorination, ethylene dichloride purification and cracking, and VCM purification steps at the same site, which probably constitute an integrated process.[3--6]

Figure III-2 shows a typical oxygen-based oxychlorination process as given in the literature. For a balanced process plant the direct chlorination and purification steps are the same as those shown in Fig. III-1 and therefore are not shown again in Fig. III-2. Ethylene (Stream 1) is fed in large excess of stoichiometric requirements, e.g., 2 to 3 times the amount needed to fully consume the hydrogen chloride (HCl) feed (Stream 2). Oyxgen (Stream 3) is also fed to the reactor, which may be either a fixed bed or a fluid bed. After passing through the oxychlorination reactor and quench area, the reaction products (Stream 4) go to a knockout drum, where the condensed crude ethylene dichloride and water (Stream 5) produced by the oxychlorination reaction are separated from the unreacted ethylene and the inert gases (Stream 6), e.g., carbon dioxide, carbon monoxide, nitrogen, argon, and nonreactive hydrocarbons, which enter the reactor as impurities with the feed streams or are formed during the oxychlorination reaction itself. From the knockout drums the crude ethylene dichloride and water (Stream 5) go to a decanter, where wastewater (Stream 7) is separated from the crude ethylene dichloride (Stream 8)

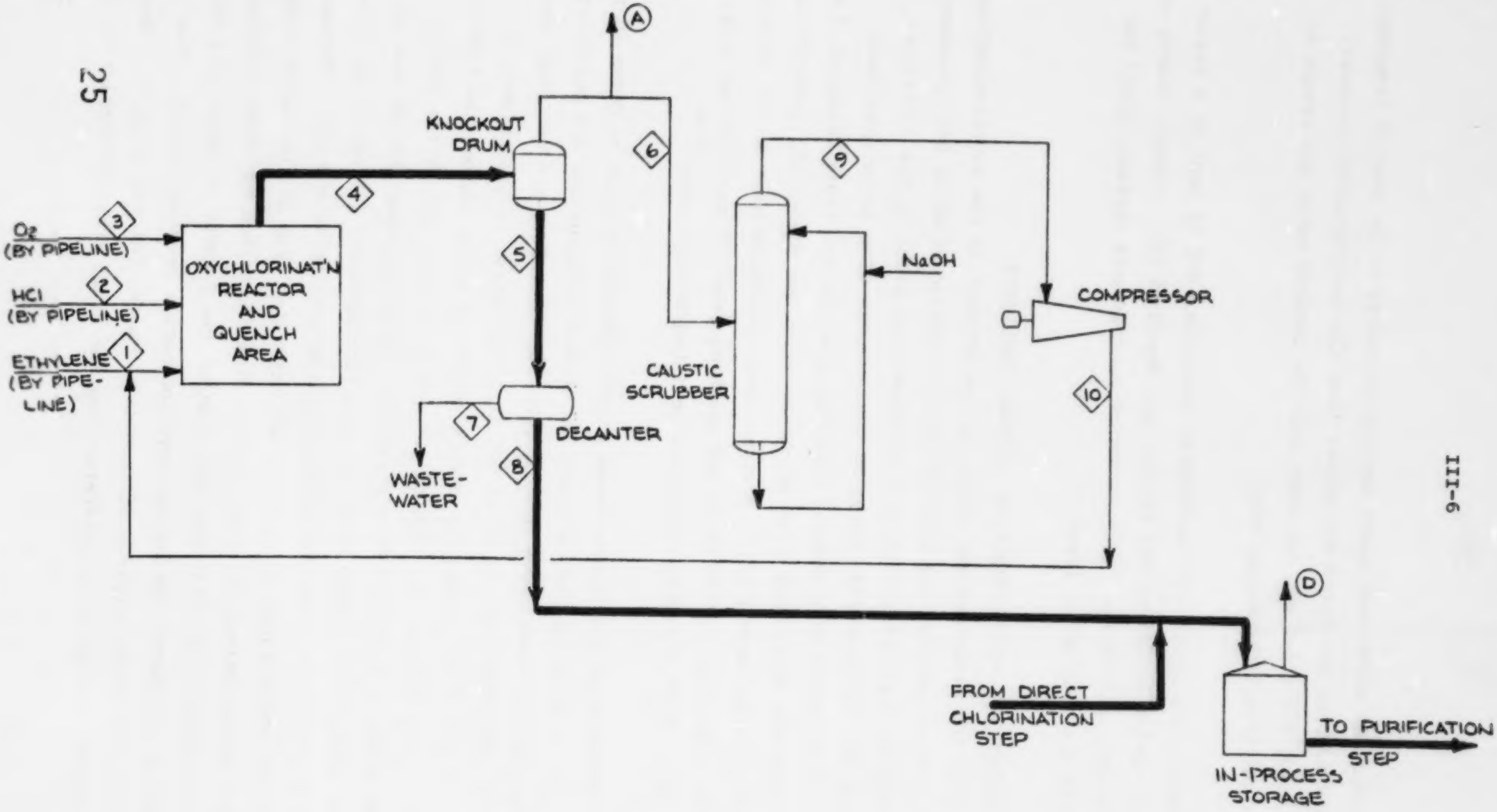
O_2
(BY PIPELINE)
3
HCl
(BY PIPELINE)
2
ETHYLENE
(BY PIPE-LINE)
1
OXYCHLORINAT'N REACTOR AND QUENCH AREA
4
KNOCKOUT DRUM
A
5
6
DECANTER
7
WASTE-WATER
8
CAUSTIC SCRUBBER
9
NaOH
COMPRESSOR
10
FROM DIRECT CHLORINATION STEP
D
IN-PROCESS STORAGE
TO PURIFICATION STEP

Fig. III-2. Ethylene Dichloride by Oxygen Process, Oxychlorination Step

which goes to in-process storage as in the air-based process. The wastewater (Stream 7) is sent to the steam stripper in the direct-chlorination step for recovery of dissolved organics.[3,4]

The vent gases (Stream 6) from the knockout drum go to a caustic scrubber for removal of hydrogen chloride and carbon dioxide. The purified vent gases (Stream 9) are then compressed and recycled (Stream 10) to the oxychlorination reactor as part of the ethylene feed.[3,4]

A small amount of the vent gas (Vent A) from the knockout drum is purged to prevent buildup of the inert gases entering with the feed streams or formed during the reaction.[3,4]

D. PROCESS VARIATIONS

Although all ethylene dichloride is produced either by direct chlorination of ethylene or by oxychlorination of ethylene, there are many variations in the reactors, recovery methods, and purification trains. However, while the general differences are well known and documented,[2--4,7,8] the details are considered to be trade secrets by the various manufacturers of ethylene dichloride.

The oxychlorination reactor may be either a tubular fixed-bed type with the catalyst inside the tubes and the coolant in the shell or a fluid-bed type with internal cooling coils. The reactor effluent may be cooled by indirect heat exchange to condense the ethylene dichloride. In one process chlorine is added to the vent gases, which are then passed through one or more catalytic reactors for removal of unreacted ethylene by conversion to ethylene dichloride. When absorption/stripping is used for recovery of ethylene dichloride from the vent gases, the absorbent may be either water or an aromatic solvent. Refrigerated vent condensers may be used to cool the oxychlorination vent gases to as low as -23°C for recovery of chlorinated hydrocarbons.[2--5,7,8]

The direct chlorination of ethylene with chlorine may be carried out either in the vapor phase or in the liquid phase. The catalyst may be a metallic chloride such as ferric, aluminum, copper, or antimony chloride; ferric chloride in a liquid-phase reactor is used by almost all commercial plants. The vapors may be condensed by water-cooled and/or refrigerated condensers or they may be absorbed in water or dilute caustic.[1,2,8]

The crude ethylene dichloride from the oxychlorination step may be combined with that from the direct chlorination and washed with water or caustic or both. The crude ethylene dichloride may be used without purification in many applications; in other applications it may be purified and may include recycled EDC from the VCM purification step.[5,7,8]

Production of other chlorinated hydrocarbons, such as 1,1,1-trichloroethane and 1,1,2-trichloroethane, may be integrated with ethylene dichloride--vinyl chloride plants.[9] Vent gas streams from the direct-chlorination step or other processing units may be recycled to the oxychlorination reactor as part of the feed to utilize the raw materials contained in the streams.[7,10] These recycle streams or the ethylene, hydrogen chloride, and chlorine feeds may contain impurities, such as methane,[7] that will exit the process in the vent gases. The light chlorinated hydrocarbons recovered in the purification step may be used as feed to perchloroethylene and carbon tetrachloride plants or may be further purified for recovery of specific chlorinated hydrocarbons. The heavy chlorinated hydrocarbons may also be processed for recovery of some of the chlorinated hydrocarbons.[5,7]

E. REFERENCES*

1. J. L. Blackford, "Ethylene Dichloride," p. 651.5932A in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (November 1975).

2. R. G. Bellamy and W. A. Schwartz, Houdry Div., Air Products and Chemicals, Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry. Volume 8: Vinyl Chloride Manufacture by the Balanced Process, EPA-450/3-73-006-h, Research Triangle Park, NC (July 1975).

3. W. E. Wimer and R. E. Feathers, "Oxygen Gives Low Cost VCM," Hydrocarbon Processing 55(3), 81--84 (1976).

4. P. Reich, "Air or Oxygen for VCM?" Hydrocarbon Processing 55(3), 85--89 (1976).

5. Responses to EPA requests for information on emissions from ethylene dichloride and vinyl choride production facilities; see Appendix E.

6. J. A. Key, IT Enviroscience, Inc., Trip Report for Visit to Dow Chemical, USA, Freeport, TX, Sept. 20, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

7. W. A. Schwartz et al., Houdry Div., Air Products and Chemicals, Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry. Volume 3: Ethylene Dichloride Manufacture by Oxychlorination, EPA-450/3-73-006-c, Research Triangle Park, NC (November 1974).

8. J. W. Pervier et al., Houdry Div., Air Products and Chemicals, Survey Reports on Atmospheric Emissions from the Petrochemical Industry, Volume II, EPA-450/3-73-005-b, Research Triangle Park, NC (April 1974).

9. Standard Support and Environmental Impact Statement: Emission Standard for Vinyl Chloride, EPA-450/2-75-009, Research Triangle Park, NC (October 1975).

10. W. M. Reiter, Allied Chemical Corporation, letter dated May 16, 1978, in response to EPA's request for information on emission data on ethylene dichloride production facilities.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation. It should be noted that although ethane is included in VOC emission totals in this report, it does not, based on current research data, participate in ozone-forming reactions to an appreciable extent.

A. DIRECT-CHLORINATION AND OXYCHLORINATION (AIR) PROCESSES

1. Model Plant

The model plant* for the balanced process (Fig. III-1) has an ethylene dichloride (ECD) capacity of 400,000 Mg/yr, based on 8760 hr of operation annually;** 215,000 Mg/yr is produced by direct chlorination and 185,000 Mg/yr by oxychlorination with air. A small quantity (8000 Mg/yr) of liquid-waste chlorinated hydrocarbons is produced and then burned in a liquid-waste incinerator. These liquid wastes could be used or sold. If there is no demand, they would be burned. The model plant is typical of several existing ethylene dichloride plants.[1]

Typical in-process, product, and waste by-product storage-tank capacities are estimated for the 400,000-Mg/yr plant. The storage-tank parameters are given in Sect. IV.A.2.d, and estimates of potential fugitive emission sources are given in Sect. IV.A.2.e. Characteristics of the model plant that are important in air-dispersion modeling are given in Table B-1 in Appendix B.

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*See p I-2 for a discussion of model plants.

**Process downtime is normally expected to range from 5 to 15%. If the hourly production rate remains constant, the annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint cost-effectiveness calculations, the error introduced by assuming continuous operation is negligible.

Process emissions from the model plants are based on emission data included in trip reports, responses to EPA letters requesting information from sites not visited, and the Houdry reports.[1,2] Nonconfidential information from emission inventory questionnaires submitted to the Texas Air Control Board and the Louisiana Air Control Commission was also used as an emission data source. Literature sources, such as the SRI Chemical Economics Handbook and the Kirk-Othmer Encyclopedia of Chemical Technology, were utilized to gain a better understanding of process unit operations and process chemistry. The data on emissions from individual distillation columns were generally not available and the data on distillation emissions that were given showed wide variations.

2. Sources and Emissions

Emission rates and sources for the balanced process based on air are summarized in Table IV-1.

a. Oxychlorination Vent -- The oxychlorination vent gas (Vent A, Fig. III-1) contains nitrogen and unreacted oxygen from the air fed to the reactor; ethane and unreacted ethylene from the ethylene feed; and the ethylene dichloride product, other chlorinated hydrocarbons, and carbon oxides produced in the reactor and not removed from the vent gases in the absorber. Table IV-2 gives the composition of this stream based on an average of data from several sources[1] but is not representative of actual data from any specific plant or process. The data points show such wide scatter that no composition can be found that is typical for either fluid-bed or fixed-bed reactors. It appears that operating conditions may influence the vent gas composition more than reactor configuration. Although there are more inert gases (nitrogen, oxygen, and carbon oxides) in the fluid-bed vent gas and more total vent gas per kg of ethylene dichloride produced than for the fixed-bed case, for both reactors the ratios of total VOC and EDC emitted per kg of EDC produced have the same ranges and averages. The ethane content of the vent gas from the model plant is calculated based on ethylene containing 0.1% ethane and on ethane being neither consumed nor produced in the oxychlorination reactor. Only inert gases are contained in the hydrogen chloride feed used in the model plant; therefore methane does not appear in the oxychlorination vent gas.

b. Direct-Chlorination Vent -- The vent gases from the direct-chlorination step (Vent B, Fig. III-1) are primarily the inert gases from the ethylene and chlorine

Table IV-1. Uncontrolled Emissions of EDC and Total VOC from Model Plants

Emission Source	Vent or Source Designation (Figs. III-1,2)	Emissions: Ratio[a] (g/kg) EDC	Emissions: Ratio[a] (g/kg) Total VOC	Emissions: Rate (kg/hr) EDC	Emissions: Rate (kg/hr) Total VOC
Oxychlorination vent					
Air process	A	3.24	7.17	148	327
Oxygen process	A[b]	0.462	9.39	21.1	429
Direct-chlorination vent	B	1.08	2.84	49.1	130
Column vents	C	3.00	13.0	137	594
Storage vents					
In-process	D	0.0149	0.0149	0.679	0.679
Product	E	0.0733	0.0733	3.34	3.34
Liquid waste	F		0.0295		1.35
Tar	G		0.000818		0.0373
Fugitive	H	0.265	0.533	12.1	24.3
Secondary					
Wastewater treatment	I	0.0181	0.0272	0.829	1.24
Incinerator	J		0.190		8.68
Total for air process		7.7	24	350	1100
Total for oxygen process		4.9	26	220	1200

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[a] g of emission per kg of EDC produced by balanced process.

[b] See Fig. III-2 for this vent source; see Fig. III-1 for all others.

Table IV-2. Composition of Model-Plant Oxychlorination (Air) Vent Gas

Component	Composition (wt %)	Emission Ratio[a] (g/kg)
Ethylene dichloride	0.81	7.0
Ethylene	0.61	5.3
Ethane	0.03	0.3
Other VOC[b]	0.34	2.9
Nitrogen	89.24	770.1
Oxygen	5.33	46.0
Carbon dioxide	2.79	24.1
Carbon monoxide	0.85	7.3
Total	100.00	863.0

[a] g of emission per kg of ethylene dichloride produced by oxychlorination.

[b] Ethyl chloride, VCM, and other chlorinated hydrocarbons. VCM concentration meets current EPA emission standards.

feeds, unreacted ethylene, and ethylene dichloride not condensed in the cooler. The ethylene dichloride in the vent gases is estimated to be 2 g/kg of the ethylene dichloride produced from the direct-chlorination step. The ethylene feed to the model plant contains 0.1% ethane, which exits with the vent gases along with the unreacted ethylene. The chlorine to the model-plant reactor consists of 0.5% inert gases, or 3.65 g/kg of direct-chlorination product, which is a significant portion of the vent emissions.

c. Column Vents -- The vent gases from the EDC stripper, the wastewater stripper, the drying column, the heads column, and the EDC finishing column (Vents C, Fig. III-1) are the noncondensables that are dissolved in the feed to the columns, the VOC that are not condensed, and, for the columns operated under vacuum, the air that leaks into the column and is removed by the vacuum jet systems. An estimate was made of the quantity of these emissions, since the available data are scarce and vary widely.[1,2]

d. Storage and Handling Emissions -- Emissions result from the storage of ethylene dichloride, in-process, and liquid-waste streams. Sources for the model plant are shown in Fig. III-1 (Sources D through G). Storage tank parameters for the model plant are given in Table IV-3. The calculated emissions in Table IV-1 are based on fixed-roof tanks, half full, and an 11°C diurnal temperature variation. Emission equations from AP-42 were used with one modification. The breathing losses were divided by 4 to account for recent evidence that indicates the AP-42 breathing-loss equation overpredicts emissions.[3,4]

No handling emissions occur in the model plant, as all raw materials, product, and waste by-products are transported by pipeline. This may not be the case in existing plants, where loading and unloading operations could result in additional emissions.

e. Fugitive Emissions -- Process pumps, process valves, and pressure relief devices are potential sources of fugitive emissions (Source H). The model plant is estimated to have 42 pumps handling VOC, 38 of which handle ethylene dichloride or other light liquids. There are an estimated 1200 process valves and 40 pressure relief devices in VOC service, with 200 process valves and 40 pressure relief

Table IV-3. Model-Plant Storage Tank Data

Storage Tank	Contents	No. of Tanks Required	Tank Size (m^3)	Turnovers (Per Year)	Bulk Temperature (°C)
In-process storage	Crude EDC	1	1140	6*	27
Liquid-waste storage	Light ends	1	380	8	27
Tar storage	Heavy ends	1	380	8	27
Product	EDC	1	3800	12*	27

*These tanks operate at approximately constant level, and the number of turnovers indicated is an attempt to account for slight level variations.

devices in gas/vapor service and 900 process valves in ethylene dichloride or other light-liquid service. The fugitive-emission factors from Appendix C were applied to these estimates, and the totals are shown in Table IV-1 as uncontrolled fugitive emissions.

f. Secondary Emissions -- Secondary emissions can result from the handling and disposal of process waste-liquid streams. Two potential sources (I and J) are indicated in Fig. III-1 for the model plant.

The secondary emissions from wastewater treatment (Source I) were estimated by procedures that are discussed in an EPA report.[5] An estimate of wastewater composition and flow rate was made, based on data received from ethylene dichloride producers.[1] A Henry's-law constant was then calculated for the vapor-liquid system under consideration, and the emission rate was estimated by comparison with information given in existing literature, such as an article by Thibodeaux.[6] This emission rate is shown in Table IV-1.

The secondary emissions of total VOC in the flue gases from the liquid chlorinated hydrocarbon incinerator (Source J) were estimated as 1% of feed. Information on these emissions is not presently available, and so the estimate was based on 99% destruction of the liquid feed. Higher than normal temperatures and residence times are required to destroy 99% or more of a liquid chlorinated hydrocarbon feed that contains no salts or solids except for a small amount of finely divided carbon. Before the flue gases are vented to the atmosphere, they are normally sent first to absorbers for recovery of HCl and then to a dilute caustic scrubber to remove unrecovered HCl and any chlorine formed in the incineration. The dilute recovered HCl may be concentrated to anhydrous HCl, which can be used as feed to the oxychlorination reactor.[2]

B. DIRECT-CHLORINATION AND OXYCHLORINATION (OXYGEN) PROCESSES

1. Model Plant

In the model-plant oxychlorination (oxygen) process (Fig. III-2) for producing ethylene dichloride, oxygen is fed to the reactor instead of air. All the capacities for both model plants are identical, i.e., 400,000 Mg/yr of ethylene dichloride from the plant, with 185,000 Mg/yr being produced by the oxychlorination step, etc. Figure III-2 shows only the oxychlorination step. Storage tank requirements and estimates of potential fugitive emission sources and secondary emission sources are also the same as for the air process. Characteristics of the model plant that are important in air dispersion modeling are given in Table B-2 in Appendix B.

2. Sources and Emissions

Emission rates and sources for the balanced ethylene dichloride process based on oxygen are summarized in Table IV-1.

a. Oxychlorination Vent -- The oxychlorination vent gas (Vent A, Fig. III-2) acts as a purge stream to prevent buildup of impurities in the recycle stream (Stream 6, Fig. III-2). These impurities are the carbon oxides, nitrogen, argon, or nonreactive hydrocarbons that enter the reactor with the feed streams or that are formed during the oxychorination reaction itself. Table IV-4 gives the composition of this stream based on an average of data from oxygen based processes[1] but is not representative of actual data from any specific process. The ethane content of the vent gas from the oxygen-based model plant is calculated based on ethylene containing 0.1% ethane and on no ethane being consumed or produced in the oxychlorination reactor. Since the ethylene and hydrogen chloride feed to the model plant contains no methane, no methane is present in these vent gases.

b. Other Emissions -- All other emissions from the the oxygen process are identical to those from the process based on air and are discussed in Sect. IV.A.2.

C. CURRENT EMISSIONS

An estimate of the 1978 emissions from the industry is 11,000 Mg/yr of ethylene dichloride and 34,000 Mg/yr of total VOC, based on an estimated 1978 level of ethylene dichloride production of 4,900,000 Mg/yr obtained by applying a 5% growth rate to the reported 1977 production of 4,679,000 Mg/yr.[7] These emission estimates are based on engineering judgement and data from individual ethylene dichloride producers, state and local emission control agencies, and the open literature. The following individual estimated projections were made:

Table IV-4. Composition of Model-Plant Oxychlorination (Oxygen) Vent Gas

Component	Composition (wt %)	Emission Ratio[a] (g/kg)
Ethylene dichloride	1.5	1
Ethylene	27.6	18
Ethane	0.5	0.3
Other VOC[b]	1.5	1
Nitrogen	15.3	10
Oxygen	3.1	2
Carbon dioxide	45.9	30
Carbon monoxide	4.6	3
Total	100.0	65.3

[a] g of emission per kg of ethylene dichloride produced by oxychlorination.

[b] Ethyl chloride, VCM, and other chlorinated hydrocarbons.

Source	1978 Emissions (Mg/yr) EDC	1978 Emissions (Mg/yr) Total VOC
Process	10,600	33,200
Storage and handling	280	310
Fugitive	60	120
Secondary	90	600
Total (rounded)	11,000	34,000

D. REFERENCES*

1. Responses to EPA requests for information on ethylene dichloride emissions; see Appendix E.

2. W. A. Schwartz et al., Houdry Div., Air Products and Chemicals, Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry. Volume 3: Ethylene Dichloride Manufacture by Oxychlorination, EPA-450/3-73-006-c, Research Triangle Park, NC (November 1974).

3. C. C. Masser, "Storage of Petroleum Liquids," Sect. 4.3 in Compilation of Air Pollutant Emission Factors, AP-42, Part A, 3d ed. (April 1977).

4. E. C. Pulaski, TRW, Inc., letter dated May 30, 1079, to Richard Burr, EPA.

5. J. J. Cudahy and R. L. Standifer, IT Enviroscience, Inc., Secondary Emissions (June 1980) (EPA/ESED report, Research Triangle Park, NC).

6. L. J. Thibodeaux, "Air Stripping of Organics from Wastewater. A Compendium," pp. 358--378 in The Proceedings of the Second National Conference on Complete Watereuse. Water's Interface with Energy, Air and Solids, Chicago, IL, May 4--8, 1975, sponsored by AIChE and EPA Technology Transfer.

7. "Manual of Current Indicators--Supplemental Data," p 219 in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (June 1978).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. APPLICABLE CONTROL SYSTEMS

A. DIRECT-CHLORINATION AND OXYCHLORINATION (AIR) PROCESSES

1. Oxychlorination Vent

The gases from the oxychlorination vent can be thermally oxidized to effectively control the ethylene dichloride (EDC) and VOC in them. Because of the large percentage of nitrogen and carbon dioxide in the vent gases, supplemental fuel must be added for proper combustion. The flue gases from the thermal oxidation of chlorine containing compounds will contain hydrogen chloride (HCl) and a small amount of chlorine, depending on operating temperature, that must be removed before the flue gases are discharged to the atmosphere. The model-plant thermal oxidizer operates at 1200°C and a residence time of 0.75 sec and has a quench chamber with water sprays to remove the HCl and a tail-gas scrubber to remove any remaining HCl and any chlorine before the flue gases are discharged from the stack. The water from the quench chamber and tail-gas scrubber is neutralized with caustic soda to control the pH of the system and is then recycled. A purge stream to waste treatment is required to prevent a buildup of dissolved solids.[1]

With a properly designed and operated thermal oxidizer a reduction of 99.9% can be achieved in ethylene dichloride and total VOC emissions. This reduction was used for calculation of the controlled emissions from the thermal oxidizer that originated in the oxychlorination vent (see Table V-1). Data to support the model-plant thermal oxidizer operating conditions are presented in an EPA report on emission control systems.[1]

Heat recovery from the thermal oxidizer flue gases can be used to produce steam to provide a credit. Experience with thermal oxidation and heat recovery of vent gases containing chlorinated hydrocarbons is limited but has revealed several problems. The flue gases are corrosive at some temperature conditions. The thermal oxidizer and heat recovery equipment must be operated carefully to prevent the occurrence of the corrosive conditions, especially on startup and shutdown of the unit.[1] One indication of the severity of these problems is the installation by Diamond Shamrock of two parallel, full-capacity, thermal oxidizer systems with heat recovery in their new VCM plant to ensure an on-stream factor of greater than 98%.[2]

Table V-1. EDC and Total VOC Controlled Emissions for Model Plants

Emission Source	Vent or Source Designation (Figs.III-1,2)	Control Device or Technique	Emission Reduction (%)	Emissions Ratio (g/kg)[a] EDC	Emissions Ratio (g/kg)[a] Total VOC	Emissions Rate (kg/hr) EDC	Emissions Rate (kg/hr) Total VOC
Oxychlorination vent							
Air process	A	Thermal oxidizer	99.9	0.00324	0.00717	0.148	0.327
Oxygen process	A[b]	Thermal oxidizer	99.9	0.000462	0.00939	0.0211	0.429
Direct-chlorination vent	B	Thermal oxidizer	99.9	0.00108	0.00284	0.0491	0.130
Column vents	C	Thermal oxidizer	99.9	0.00300	0.0130	0.137	0.594
Storage vents							
In-process	D	Refrigerated condenser	85	0.00223	0.00223	0.102	0.102
Product	E	Refrigerated condenser	85	0.0110	0.0110	0.502	0.502
Liquid waste	F	Refrigerated condenser	82		0.00525		0.240
Tar	G	None			0.000818		0.0373
Fugitive	H	Detection and correction of major leaks	72	0.0743	0.149	3.39	6.79
Secondary							
Wastewater treatment	I	None		0.0181	0.0272	0.829	1.24
Incinerator	J	Change operating conditions	100		Not detectable		
Total for air process				0.11	0.22	5.2	10
Total for oxygen process				0.11	0.22	5.0	10

[a] kg of emission per kg of EDC produced by balanced process.

[b] See Fig. III-2 for this source; see Fig. III-1 for all other sources.

Two thermal oxidizers for the direct-chlorination and oxychlorination (air) model plant were studied: one with heat recovery to produce steam and one without heat recovery. Both cases have the same emission reduction efficiency, but differ in the size of the quench chamber, caustic scrubber, fan, and pumps because of the different flue-gas temperatures to the quench chamber that result in different flue gas volumes to be quenched and scrubbed and in different amounts of water that are evaporated.

Several other alternative thermal oxidizer configurations are possible, both with and without heat recovery. An acid scrubber may be used instead of a water quench to recover dilute hydrochloric acid, which may be used in other processes for its acidity or may be neutralized with a cheaper base than caustic soda. Other systems may be used to recover hydrochloric acid at higher concentrations, as well as anhydrous hydrogen chloride.[3,4] The thermal oxidizer may be designed to burn both vent gases and liquid chlorinated by-products.[5]

Catalytic oxidation is also used to control emissions from an oxychlorination vent. The unit reportedly does remove carbon monoxide and ethylene with better than 99.7% reduction; however, it removes less than 75% of the ethylene dichloride and less than 60% of the VCM, with 100 ppm of ethylene dichloride and 8 ppm of VCM remaining in the stack gases.[6]

Another device that reduces the ethylene in the oxychlorination vent gases is a "post" reactor, where chlorine is added to chlorinate the residual ethylene to ethylene dichloride. Reportedly complete ethylene conversion is obtained, with the residual concentration in the vent gas being as low as 10 ppm of ethylene.[7] Data from a plant using this technology show only 0.02 wt % of ethylene but 0.75 wt % of ethylene dichloride and 2 wt % of total VOC in the vent gas after it has been refrigerated to subzero temperature and then scrubbed with water.[8]

Other devices, such as refrigerated vent condensers and hydrocarbon or chilled water absorbers, do remove some ethylene dichloride and total VOC from the vent gas; however, they allow significant quantities to go to the atmosphere.[8]

2. Direct-Chlorination Vent

The emissions from the direct-chlorination vent can be controlled by piping them to the thermal oxidizer used for controlling the oxychlorination vent gas as discussed in Sect. A.1 or to a vapor and liquid thermal oxidizer serving other processing units.[8] A reduction of 99.9% was used in the calculations of the controlled emissions from the thermal oxidizer that originate in the direct-chlorination vent (see Table V-1).

Other devices that may be used to control the emissions from the direct-chlorination vent are refrigerated vent condensers, scrubbers, and flares, or a combination of these, depending on the composition of the vent gases. If properly designed, a refrigerated vent condenser is effective for removal of ethylene dichloride (approximately 96% if the vent gases are cooled from 35°C to -26°C at 240 kPa), although the unreacted ethylene and ethane will remain. Scrubbers may absorb some ethylene dichloride depending on the operating conditions, but are primarily installed for removal of hydrogen chloride and unreacted chlorine.[8]

3. Column Vents

The emissions from the column vents can also be effectively controlled by piping them to the thermal oxidizer used for controlling the emissions from the oxychlorination and direct-chlorination vents or to a vapor and liquid thermal oxidizer serving other processing units.[1,3] A reduction of 99.9% was used in the calculations of the controlled emissions from the thermal oxidizer that originated in the column vents (see Table V-1).

The same devices discussed above for the direct-chlorination vent are used to control the gases from the column vents and the same conditions apply to their use and effectiveness. These emissions are caused by inert gases that are dissolved in the column feeds and that leak into the vacuum columns, and the quantity varies widely.[8] The amount of these inert gases can have a considerable impact on the reduction efficiency of a refrigerated vent condenser, as discussed in Sect. A-2.

4. Storage Vents

According to information received from companies producing ethylene dichloride, the crude ethylene dichloride, the product ethylene dichloride, the lights, and the heavies are stored in fixed-roof tanks. Often the crude ethylene dichloride is stored under a water layer, which will reduce the emissions somewhat. A nitrogen blanket is sometimes employed to keep the product ethylene dichloride dry. Emissions are controlled by using refrigerated vent condensers or by piping the storage tank vents to a thermal oxidizer.[8]

The emissions from the model-plant storage tanks are controlled by use of refrigerated vent condensers except for the tar storage tank, which is uncontrolled. Reportedly no materials for floating-roof seals are available for use with EDC.[9] Options for control of storage emissions are covered in another EPA report.[10]

The controlled storage emissions were estimated based on vent condensers operating at -10°C and on recovery of 85% of the EDC from the vents on the in-process storage tanks and on the product storage tanks. An estimated 82% recovery is calculated for the liquid-waste storage tank (see Table V-1).

5. Fugitive Emissions

Controls for fugitive emissions from the synthetic organic chemicals manufacturing industry are discussed in a separate EPA document.[11] Emissions from pumps, process valves, and pressure relief devices can be controlled by an appropriate leak-detection system and with repair and maintenance as needed. Controlled fugitive emissions were calculated with the appropriate factors given in Appendix C and are included in Table V-1.

6. Secondary Emissions

a. Wastewater Treatment -- Calculations based on estimated wastewater flow rates and compositions for the model plant indicate that the emissions from the wastewater treatment are relatively small. No control system has been identified for the model plant.

b. Liquid Chlorinated Hydrocarbon Incinerator -- Control of the secondary emissions from the liquid chlorinated hydrocarbon incinerator consists of changing the incinerator operating conditions. Data on the relationship of emissions to operating conditions are not available at this time. Some information indicates that higher temperatures and longer residence times are probably helpful in reducing these secondary emissions.[3,12–14] Levels of organic chlorides in the flue gases from the liquid chlorinated hydrocarbon incinerators have been reported to be none and 30 ppm by weight.[15,16] The controlled secondary emissions from the model-plant liquid chlorinated hydrocarbon incinerator are estimated to be nondetectable, as indicated in Table V-1.

B. DIRECT-CHLORINATION AND OXYCHLORINATION (OXYGEN) PROCESSES

1. Oxychlorination Vent

The vent gases from the oxychlorination vent when oxygen is used as the feed contain much less nitrogen than when air is used and can support combustion with little or no supplemental fuel required. An emission reduction of 99.9% was used to calculate the controlled emissions from the thermal oxidizer that originated in the model-plant oxychlorination vent (see Table V-1). With a properly designed and operated thermal oxidizer, a reduction of 99.9% can be achieved in ethylene dichloride and total VOC emissions. Data to support the operating conditions of 0.75-sec residence time and of 1200°C are presented in another EPA report.[1]

Heat recovery from the thermal oxidizer flue gases can be used to produce steam. The same problems discussed in Sect. A.1 will apply to this case.

2. Other Vents

The control systems and controlled emissions for the model-plant direct-chlorination vent, column vents, storage vents, fugitive sources, and secondary sources are the same as for the air process model plant (see Table V-1).

C. REFERENCES*

1. H. S. Basdekis, IT Enviroscience, Inc., Control Device Evaluation. Thermal Oxidation Supplement (VOC Containing Halogens or Sulfur) (in preparation for EPA, ESED, Research Triangle Park, NC).

2. Texas Air Control Board, A Construction Permit...to Diamond Shamrock Chemical Company Authorizing Construction of Vinyl Chloride Plant...at La Porte, Harris County, Texas, Permit No. C-3855 (Nov. 2, 1976).

3. Y. H. Kiang, "Controlling Vinyl Chloride Emissions," Chemical Engineering Progress 72(12), 37--41 (1976).

4. C. G. Bertram, "Minimizing Emissions from Vinyl Chloride Plants," Environmental Science and Technology 11(9), 864--868 (1977).

5. J. A. Key, IT Enviroscience, Inc., Trip Report for Visit to Borden Chemical, Geismar, Louisiana, March 2, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

6. W. R. Taylor, Diamond Shamrock Corporation, Deer Park, TX, letter dated Oct. 3, 1977, to EPA in response to EPA request for information on the catalytic oxidation unit.

7. P. Reich, "Air or Oxygen for VCM?" Hydrocarbon Processing 55(3), 85--89 (1976).

8. Responses to EPA requests for information on ethylene dichloride emissions; see Appendix E.

9. F. C. Dehn, PPG Industries, Inc., letter dated Mar. 12, 1979, to EPA with comments on the draft report on ethylene dichloride.

10. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (in preparation for EPA, ESED, Research Triangle Park, NC).

11. D. G. Erikson, IT Enviroscience, Inc., Fugitive Emissions (in preparation for EPA, ESED, Research Triangle Park, NC).

12. S. B. Farbstein and J. Elder, Energy Conservation in the Chemical Industry Through New Process Development -- The B. F. Goodrich Catoxid Process, paper presented before the Federal Energy Administration Project Independence Hearing, San Francisco, CA, Oct. 7, 1974.

13. R. E. Van Ingen, Shell Oil Company, Norco, LA, letter dated Dec. 6, 1974, to EPA in response to EPA request for information on vinyl chloride monomer operations.

14. T. T. Shen et al., "Incineration of Toxic Chemical Wastes," Pollution Engineering 10(10), 45--50 (1978).

15. J. A. Mullins, Shell Oil Company, Deer Park, TX, letter dated June 22, 1978, to EPA in response to EPA request for information on ethylene dichloride manufacture.

16. J. A. Key, IT Enviroscience, Inc., Trip Report for Visit to Dow Chemical, U.S.A. Oyster Creek Division, Freeport, TX, September 20, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VI. IMPACT ANALYSIS

A. ENVIRONMENTAL AND ENERGY IMPACTS

1. Direct-Chlorination and Oxychlorination (Air) Processes

Table VI-1 shows the environmental impact of reducing the ethylene dichloride (EDC) and VOC emissions by application of the indicated control systems to the air process model plant. Use of these control devices or techniques results in the reduction of EDC emissions by 3030 Mg/yr and total VOC emissions by 9460 Mg/yr for the model plant.

a. Process Vents -- The thermal oxidizer used for control of emissions from vents A [oxychlorination (air)], B (direct chlorination), and C (column vents) (Fig. III-1) reduces the air process model plant EDC emissions by 2900 Mg/yr and total VOC emissions by 9200 Mg/yr.

The thermal oxidizer uses natural gas as supplemental fuel and electric power for the blowers, pumps, lighting, and instruments. The total energy required to operate the thermal oxidizer for the air process model plant is approximately 26 GJ/hr. If heat recovery equipment is installed and approximately 70% of the available energy from the combustion gases is recovered as steam, the amount of steam produced will be about 66 GJ/hr. Since a balanced VCM plant consumes a substantial quantity of steam above that produced in the oxychlorination reactor system, this steam can often be utilized on-site.[1,2] Because the potential exists for some companies to have excess steam on-site, it may not be practical for all companies to utilize the heat recovery option.

The combustion of chlorinated compounds in the thermal oxidizer produces hydrogen chloride (HCl) and free chlorine, which leave in the flue gases. In the removal and neutralization of these acid gases by the model plant's quench chamber, tail gas scrubber, and neutralization sump, 7600 Mg of salt in dilute solution is produced annually. Plants located near the ocean can dispose of this salt solution without major problems.[3] Others may find it more economical to use alternative systems for removal of HCl and chlorine that produce a dilute hydrochloric acid solution as discussed in Sect. V.

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Table VI-1. Environmental Impact of Controlled Ethylene Dichloride for Model Plants

Emission Source	Vent or Source Designation (Figs. III-1,2)	Control Device or Technique	Emission Reduction (%)	Emission Reduction (Mg/yr)	
				EDC	Total VOC
xychlorination vent					
Air process	A	Thermal oxidizer	99.9	1290	2,860
Oxygen process	A[a]	Thermal oxidizer	99.9	185	3,750
irect-chlorination vent	B	Thermal oxidizer	99.9	430	1,140
olumn vents	C	Thermal oxidizer	99.9	1200	5,190
torage vents					
In-process	D	Refrigerated condenser	85	5.06	5.06
Product	E	Refrigerated condenser	85	24.9	24.9
Liquid waste	F	Refrigerated condenser	82		9.7
Tar	G	None			
ugitive	H	Detection and correction of major leaks	72	76.3	153
econdary					
Wastewater treatment	I	None			
Incinerator	J		100		76.0
Total for air process				3030	9,460
Total for oxygen process				1920	10,300

[a] See Fig. III-2 for this vent source; see Fig. III-1 for all other sources.

b. Other Emissions (Storage, Fugitive, and Secondary) -- Control methods described for these sources for the model plants are refrigerated vent condensers, repair of leaking equipment for fugitive emissions, and change of operating conditions for the liquid-waste incinerator.

Application of these systems results in an EDC emission reduction of 106 Mg/yr and a VOC emission reduction of 270 Mg/yr for the model plants.

2. Direct-Chlorination and Oxychlorination (Oxygen) Processes

Table VI-1 shows the environmental impact of reducing the EDC and VOC emissions by application of the indicated control systems to the oxygen-process model plant. Application of these control devices or techniques results in the reduction of EDC emissions by 1920 Mg/yr and total VOC emissions by 10,300 Mg/yr for the model plant.

a. Process Vents -- The thermal oxidizer used for control of emissions from vent A (Fig. III-2) and vents B and C (Fig. III-1) reduces the model-plant EDC emission by 1800 Mg/yr and total VOC emissions by 10,000 Mg/yr.

The thermal oxidizer for the model plant does not require supplemental fuel, because the vent gases from the process vents are self-combustible. The energy required as electric power for the blowers, pumps, lighting, and instruments is approximately 0.25 GJ/hr. If heat recovery equipment is installed and approximately 70% of the available energy from the combustion gases is recovered as steam, about 34 GJ of steam will be produced per hour.

The removal and neutralization of the acid gases from the thermal oxidizer flue gases will produce about 5900 Mg/yr of salt from the model plant.

b. Other Emissions (Storage, Fugitive, and Secondary) -- The control methods and environmental and energy impacts for these sources in the oxygen-process model plant are identical to those of the air-process model plant; see Sect. VI.A.1.b.

B. CONTROL COST IMPACT

This section gives estimated costs and cost-effectiveness data for control of ethylene dichloride and total VOC emissions resulting from the production of ethylene dichloride. Details of the model plant (Figs. III-1 and III-2) are given in Sects. III and IV. Cost estimate sample calculations are included in Appendix D.

Capital cost estimates represent the total investment required for purchase and installation of all equipment and material needed for a complete emission control system performing as defined for a new plant at a typical location. These estimates do not include the cost of ethylene dichloride production lost during installation or startup, research and development, or land acquisition.

Bases for the annual cost estimates for the control alternatives include utilities, waste disposal, chemicals, operating labor, maintenance supplies and labor, recovery credits, capital charges, and miscellaneous recurring costs such as taxes, insurance, and administrative overhead. The cost factors used are itemized in Table VI-2.

1. Direct-Chlorination and Oxychlorination (Air) Processes

a. Process Vents -- The estimated installed capital cost of a thermal oxidizer designed to reduce by 99.9% the ethylene dichloride and total VOC from the process vents in the model plant is $2.1 million (see Table VI-3). If waste heat recovery is included to reduce the operating cost, the estimated installed capital cost is $2.7 million. These costs are based on a thermal oxidizer designed for a residence time of 0.75 sec at 1200°C, completely installed, and includes a quench chamber, tail gas scrubber, sump, pumps, blower, and stack. The use of heat recovery reduces the temperature, and therefore the volume, of the flue gases to the quench and scrubber, which consequently will be smaller.

The process-vent-gas rate varies directly with the production rate; therefore the capacity of the thermal oxidizer will depend on the capacity of the plant. Figure VI-1 was plotted to show the variation of installed capital cost of a thermal oxidizer, with and without heat recovery, versus plant capacity.

To determine the cost effectiveness of a thermal oxidizer, estimates were made of the direct operating cost, the capital recovery cost, and miscellaneous capital costs, both with and without heat recovery. The recovery credit was calculated for the heat recovery case based on recovery of approximately 70% of the energy

Table VI-2. Annual Cost Parameters

Operating factor	8760 hr/yr[a]
Operating labor	$15/man-hr
Fixed costs	
Maintenance labor plus materials, 6%	29% of installed capital cost
Capital recovery, 18%[b]	
Taxes, insurances, administration charges, 5%	
Utilities	
Electric power	$8.33/GJ ($0.03/kWh)
Natural gas	$1.90/GJ ($2.00/thousand ft^3 or million Btu)
Heat recovery credits (equivalent to natural gas)	$1.90/GJ ($2.00/million Btu)
Caustic (50% NaOH)	$0.11/kg (5¢/lb)
Makeup water	$0.026/m^3 (10¢/1000 gal)

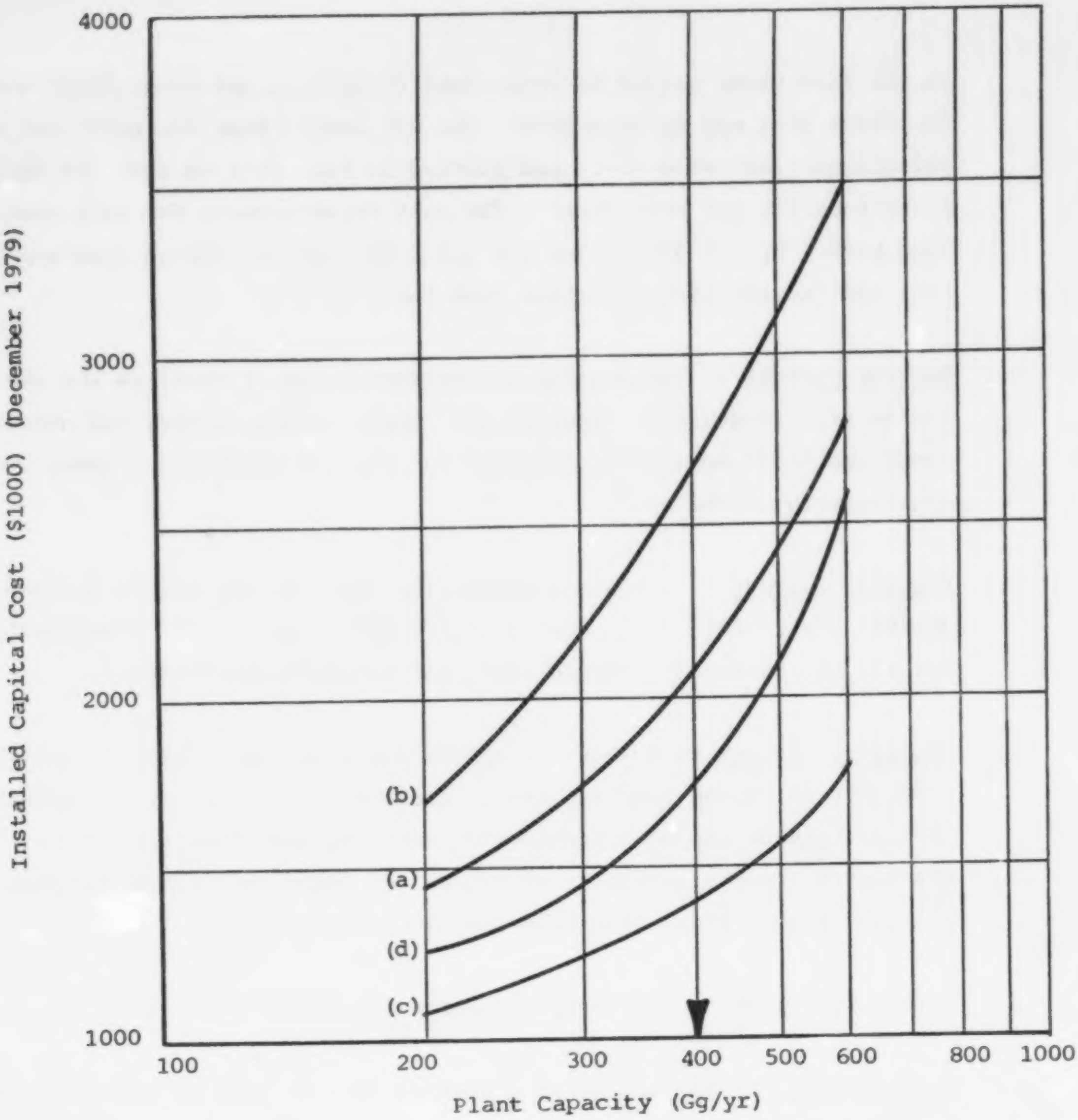
[a] Process downtime is normally expected to range from 5 to 15%. If the hourly rate remians constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation is negligible.

[b] Based on 10-year life and 12% interest.

Table VI-3. Emission Control Cost Estimates for Ethylene Dichloride Model Plants

Control	Total Installed Capital Cost	Annual Operating Costs			(B) Emission Reduction			(C)[a] Cost Effectiveness	
		Gross Annual	Recovery Credits	(A) Net Annual	EDC (Mg/yr)	Total VOC (Mg/yr)	(%)	EDC (per Mg)	Total VOC (per Mg)
		Direct-Chlorination and Oxychlorination (Air) Processes							
Thermal oxidizer									
With heat recovery	$2,700,000	$4,080,000	$1,100,000	$2,980,000	2,900	9,200	99.9	$1,028	$324
Without heat recovery	2,100,000	3,910,000	0	3,910,000	2,900	9,200	99.9	1,348	425
		Direct-Chlorination and Oxychlorination (Oxygen) Processes							
Thermal oxidizer									
With heat recovery	$1,750,000	$2,960,000	$ 560,000	$2,400,000	1,800	10,000	99.9	$1,333	$240
Without heat recovery	1,400,000	2,860,000	0	2,860,000	1,800	10,000	99.9	1,589	286

[a] (C) = (A) : (B).



(a) Thermal oxidation without heat recovery, air process
(b) Thermal oxidation with heat recovery, air process
(c) Thermal oxidation without heat recovery, oxygen process
(d) Thermal oxidation with heat recovery, oxygen process

Fig. VI-1. Installed Capital Cost vs Plant Capacity for Emission Control by Thermal Oxidation

in the flue gases valued as equivalent to natural gas at $1.90/GJ and not for the steam that may be generated. The net annual cost for each case was then calculated (see Table VI-3) and plotted in Fig. VI-2 to show the variation with plant capacity for both cases. The cost effectiveness for each case for controlling both ethylene dichloride and total VOC was calculated from the net annual cost and the emission reduction (see Table VI-3).

b. Storage Sources -- The control system for storage sources is the use of refrigerated vent condensers. Another EPA report covers storage and handling emissions and their applicable controls for all the synthetic organic chemicals manufacturing industry.[4]

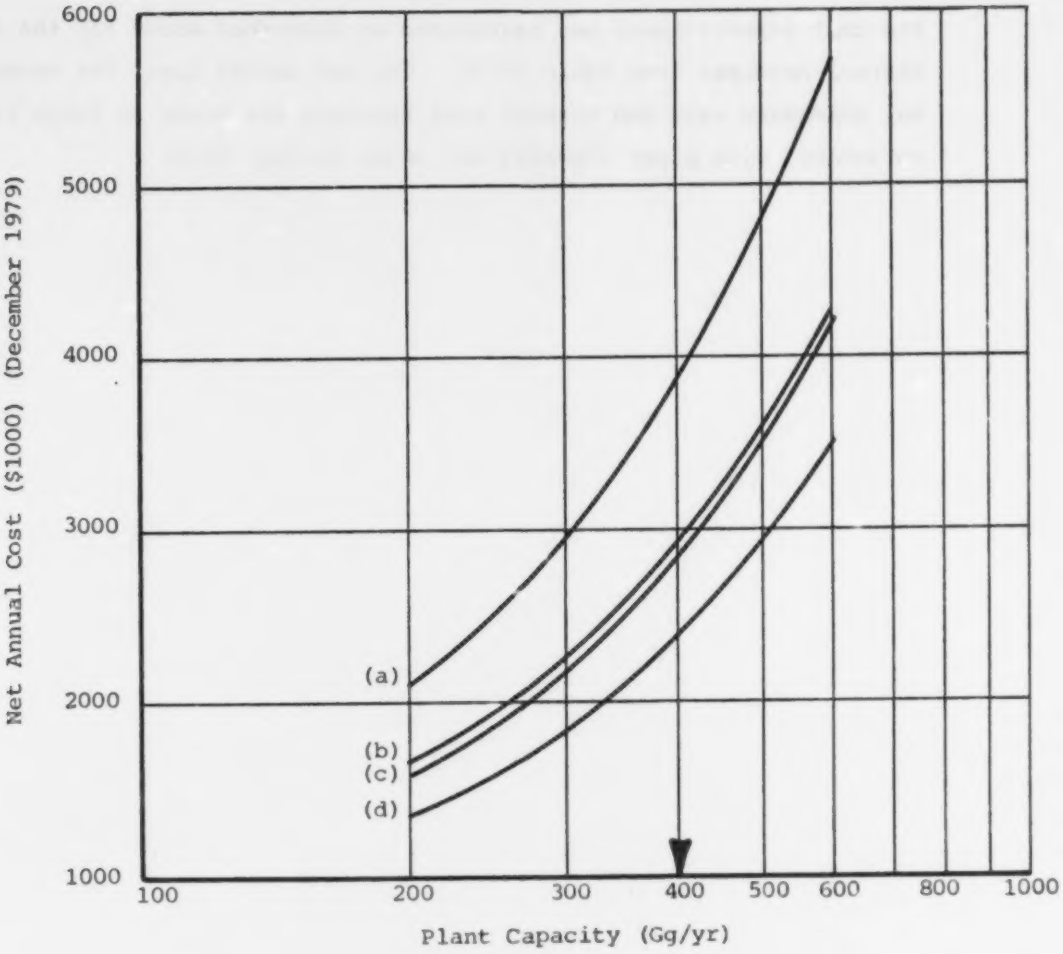
c. Fugitive Sources -- A control system for fugitive sources is defined in Appendix C. Another EPA report[5] will cover fugitive emissions and their applicable controls for all the synthetic organic chemicals manufacturing industry.

d. Secondary Sources -- No control system has been identified for controlling the secondary emissions from wastewater treatment. The secondary emissions from the incinerator can be controlled by changing operating conditions. Another EPA report[6] covers secondary emissions and their applicable controls for all the synthetic organic chemicals manufacturing industry.

2. Direct-Chlorination and Oxychlorination (Oxygen) Processes

a. Process Vents -- The estimated installed capital cost of a thermal oxidizer designed to reduce by 99.9% the ethylene dichloride and total VOC from the process vents in the oxygen-process model plant is $1.75 million with heat recovery and $1.4 without heat recovery (see Table VI-3). These costs are based on a thermal oxidizer designed for a residence time of 0.75 sec at 1200°C, completely installed, and includes a quench chamber, tail gas scrubber, sump, pumps, blower, and stack.

Figure VI-1 shows the variation of installed capital cost of a thermal oxidizer, with and without heat recovery, versus plant capacity.



(a) Thermal oxidation without heat recovery, air process
(b) Thermal oxidation with heat recovery, air process
(c) Thermal oxidation without heat recovery, oxygen process
(d) Thermal oxidation with heat recovery, oxygen process

Fig. VI-2. Net Annual Cost vs Plant Capacity for Emission Control by Thermal Oxidation

The cost effectiveness was calculated as described above for the air-process thermal oxidizer (see Table VI-3). The net annual costs for oxygen-process thermal oxidizers with and without heat recovery are given in Table VI-3 and the variations with plant capacity are shown in Fig. VI-2.

C. REFERENCES*

1. W. A. Schwartz et al., Houdry Div., Air Products and Chemicals, Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry. Volume 3: Ethylene Dichloride Manufacture by Oxychlorination, EPA-450/3-73-006-c, Research Triangle Park, NC (November 1974).

2. P. Reich, "Air or Oxygen for VCM?" Hydrocarbon Processing 55(3), 85--89 (1976).

3. C. G. Bertram, "Minimizing Emissions from Vinyl Chloride Plants," Environmental Science and Technology 11(9), 864--868 (1977).

4. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (in preparation for EPA, ESED, Research Triangle Park, NC).

5. D. G. Erikson, IT Enviroscience, Inc., Fugitive Emissions (in preparation for EPA, ESED, Research Triangle Park, NC).

6. J. J. Cudahy and R. L. Standifer, IT Enviroscience, Inc., Secondary Emissions (June 1980) (EPA/ESED report, Research Triangle Park, NC).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VII. SUMMARY

Ethylene dichloride (EDC) is produced by the direct chlorination of ethylene and by the oxychlorination of ethylene with hydrogen chloride (HCl) and oxygen or air, often in a balanced plant, where the EDC is used to make vinyl chloride monomer (VCM) and with hydrogen chloride (HCl) produced as by-product. The HCl is recycled and the ethylene dichloride product is about evenly split between the direct-chlorination step and the oxychlorination step.[1--3]

The annual growth rate of ethylene dichloride production is estimated to be 4 to 5%,[1] and production is projected to utilize 85 to 89% of 1977 capacity by 1982.

Emission sources and uncontrolled and controlled emission rates from model plants for the direct-chlorination and the oxychlorination (air and oxygen) processes are given in Table VII-1. The emissions projected for the domestic ethylene dichloride industry based on the estimated control of about 70% in 1978 are 11,000 Mg of ethylene dichloride per year and 34,000 Mg of total VOC per year. Control devices for operating plants include thermal oxidizers, catalytic oxidizers, vent condensers, scrubbers, and vent-gas post reactors. An emission reduction of 99.9% may be realized in a thermal oxidizer. The installed capital cost of a thermal oxidizer for the air-based-process model plant is $2.7 million with heat recovery and $2.1 without heat recovery; for the oxygen-based-process model plant it is $1.75 million with heat recovery and $1.4 million without heat recovery. Supplemental fuel is required for the combustion of the gases from the direct-chlorination, oxychlorination (air), and column vents but not for the oxygen-process vents because those gases contain much less nitrogen and are self-combustible.

For the thermal oxidizer on the direct-chlorination and oxychlorination (air) model-plant vents the cost effectiveness for control of ethylene dichloride is

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[1] J. L. Blackford, "Ethylene Dichloride," pp. 651.5031A--651.5033I in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (November 1975).

[2] P. Reich, "Air or Oxygen for VCM?" Hydrocarbon Processing 55(3), 85--89 (1976).

[3] W. E. Wimer and R. E. Feathers, "Oxygen Gives Low Cost VCM," Hydrocarbon Processing 55(3), 81--84 (1976).

Table VII-1. Emission Summary for Model Plants

		Emission Rate (kg/hr)			
	Vent or Source Designation	Uncontrolled		Controlled	
Emission Source	(Figs. III-1,2)	EDC	Total VOC	EDC	Total VOC
Oxychlorination vent					
For air process	A	148	327	0.148	0.327
For oxygen process	A[a]	21.1	429	0.0211	0.429
Direct-chlorination vent	B	49.1	130	0.0491	0.130
Column vents	C	137	594	0.137	0.594
Storage vents					
In-process	D	0.679	0.679	0.102	0.102
Product	E	3.34	3.34	0.502	0.502
Liquid waste	F		1.35		0.240
Tar	G		0.0373		0.0373
Fugitive	H	12.1	24.3	3.39	6.79
Secondary					
Wastewater treatment	I	0.829	1.24	0.829	1.24
Incinerator	J		8.68		
Total for air process		350	1100	5.2	10
Total for oxygen process		220	1200	5.0	10

[a] See Fig. III-2 for this source; see Fig. III-1 for all other sources.

$1028/Mg if heat is recovered and $1348/Mg if it is not. The cost effectiveness for control of total VOC is $324/Mg with heat recovery and $425/Mg without heat recovery. The cost effectiveness of the thermal oxidizer on the direct-chlorination and oxychlorination (oxygen) model-plant vents is $1333/Mg of ethylene dichloride and $240/Mg of total VOC if heat is recovered or $1589/Mg of ethylene dichloride and $286/Mg of total VOC without heat recovery. Approximately 37 GJ of steam per hour is produced from the air-process thermal oxidizer flue gases at approximately 70% recovery and about 27 GJ/hr from the oxygen-process gases at the same recovery.

APPENDIX A

PHYSICAL PROPERTIES OF EDC AND ETHYLENE

Table A-1. Physical Properties of 1,2-Dichloroethane*

Synonyms	Ethylene dichloride, ethylene chloride
Molecular formula	$C_2H_4Cl_2$
Molecular weight	99.0
Vapor pressure	84.42 mm Hg at 25°C
Melting point	-35.5°C
Boiling point	83.5°C at 760 mm Hg
Density	1.257 at 20°C/4°C
Physical state	Liquid
Vapor density	3.35
Water solubility	0.43 g/100 ml

*From: J. Dorigan *et al.*, "Ethylene Dichloride," p. AII-270 in Appendix II, Rev 1, *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Organic Chemicals (Chemicals D--E)*, MTR-7248, MITRE Corp. (September 1976).

Table A-2. Physical Properties of Ethylene[a]

Synonyms	Acetene, ethene
Molecular formula	C_2H_4
Molecular weight	28.06
Vapor pressure	34,200 mm Hg at 0°C
Melting point	-169°C
Boiling point	-103.9°C at 760 mm Hg
Density	0.99267 at 20°C/4°C
Physical state	Gas
Vapor density	0.98
Water solubility	Insoluble

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[a] From J. Dorigan *et al*., "Ethylene," p. AII-260 in Appendix II, Rev. 1, *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Organic Chemicals (Chemicals D--E)*, MTR-7248, Mitre Corp. (September 1976).

APPENDIX B

AIR-DISPERSION PARAMETERS

Table B-1. Air-Dispersion Parameters for Ethylene Dichloride Model Plants (Air) (Capacity, 400,000 Mg/yr), Controlled and Uncontrolled

Source	Emission Rate (g/sec) EDC	Emission Rate (g/sec) Total VOC	Tank Height (m)	Tank Diameter (m)	Stack Height (m)	Stack Diameter (m)	Discharge Temperature (K)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
				Uncontrolled Emissions					
Oxychlorination vent	41.1	90.9			50	0.6	300	4.34	15.4
Direct-chlorination vent	13.6	36.1			30	0.1	300	0.0419	5.34
Column vents	38.1	165			20	0.2	300	0.218	6.94
Storage vents									
In-process	0.19	0.19	9.8	12.2			300		
Product	0.93	0.93	12.2	19.9			300		
Liquid waste		0.37	9.8	7.0			300		
Tar		0.010	9.8	7.0			300		
Fugitive	3.36	6.75[a]							
Secondary									
Wastewater treatment	0.23[b]	0.34[b]							
Incinerator		2.41			30	0.6	340	1.45	5.12
				Controlled Emissions					
Thermal oxidizer with heat recovery	0.0929 0.0929	0.292 0.292			30	1.0	330	10.4	13.2
Thermal oxidizer without heat recovery					30	1.2	350	15.6	13.8
Storage vents									
In-process	0.028	0.028	9.8	12.2			300		
Product	0.14	0.14	12.2	19.9			300		
Liquid waste		0.067	9.8	7.0			300		
Fugitive	0.94[a]	1.89[a]							
Secondary									
Incinerator		N.D.[c]			30	0.6	340	1.45	5.12

[a] Distributed over an area of 100 m by 200 m.

[b] No control specified.

[c] None detectable.

Table B-2. Air-Dispersion Parameters for Ethylene Dichloride Model Plant (Oxygen) (Capacity, 400,000 Mg/yr), Controlled and Uncontrolled

Source	Emission Rate (g/sec)		Tank Height (m)	Tank Diameter (m)	Stack Height (m)	Stack Diameter (m)	Discharge Temperature (K)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
	EDC	Total VOC							
Uncontrolled Emissions									
Oxychlorination vent	5.87	119			50	0.2	300	0.272	8.7
Direct-chlorination vent	13.6	36.1			30	0.1	300	0.0419	5.34
Column vents	38.1	165			20	0.2	300	0.218	6.94
Storage vents									
In-process	0.19	0.19	9.8	12.2			300		
Product	0.93	0.93	12.2	19.9			300		
Liquid waste		0.37	9.8	7.0			300		
Tar		0.010[b]	9.8	7.0			300		
Fugitive	3.36[a]	6.75[a]							
Secondary									
Wastewater treatment	0.23[b]	0.34[b]							
Incinerator		2.41			30	0.6	340	1.45	5.12
Controlled Emissions									
Thermal oxidizer with heat recovery	0.0576	0.320			30	0.9	330	7.36	11.6
Thermal oxidizer without heat recovery	0.0576	0.320			30	1.0	350	11.0	14.0
Storage vents									
In- process	0.028	0.028	9.8	12.2			300		
Product	0.14	0.14	12.2	19.9			300		
Liquid waste		0.067	9.8	7.0			300		
Fugitive	0.94[a]	1.89[a]							
Secondary									
Incinerator		N.D.[c]			30	0.6	340	1.45	5.12

[a] Distributed over an area of 100 m by 200 m.

[b] No control specified.

[c] None detectable.

APPENDIX C

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX D

COST ESTIMATE SAMPLE CALCULATIONS

This appendix contains sample calculations showing how costs presented in this report were estimated.

The accuracy of an estimate is a function of the degree of data available when the estimate was made. Figure D-1 illustrates this relationship. A contingency allowance as indicated on this chart has been included in the estimated costs to cover the undefined scope of the project.

Capital costs given in this report are based on a screening study, as indicated by Fig. D-1, based on general design criteria, block flowsheets, approximate material balances, and data on general equipment requirements. These costs have an accuracy range of +30% to -23%, depending on the reliability of the data, and provide an acceptable basis to determine the most cost-effective alternate within the limits of accuracy indicated.

A. THERMAL OXIDIZER CONTROLLING EMISSIONS FROM MODEL PLANT USING THE OXYCHLORINATION WITH AIR PROCESS

This example is based on the estimated emissions of 8900 scfm, with a heat content of 50 Btu/scf going to a thermal oxidizer operated at 2200°F with 0.75-sec residence time and equipped with heat recovery. The estimated emissions include the vent gases from the oxychlorination vent, from the direct-chlorination vent, and from the distillation vents and have the following compositions:

Component	Composition (mole %)
EDC	0.50
Ethylene	0.98
Other chlorinated hydrocarbons	1.19
Ethane	0.07
Carbon monoxide	1.43
Carbon dioxide	2.03
Oxygen	4.90
Nitrogen	88.90

C7

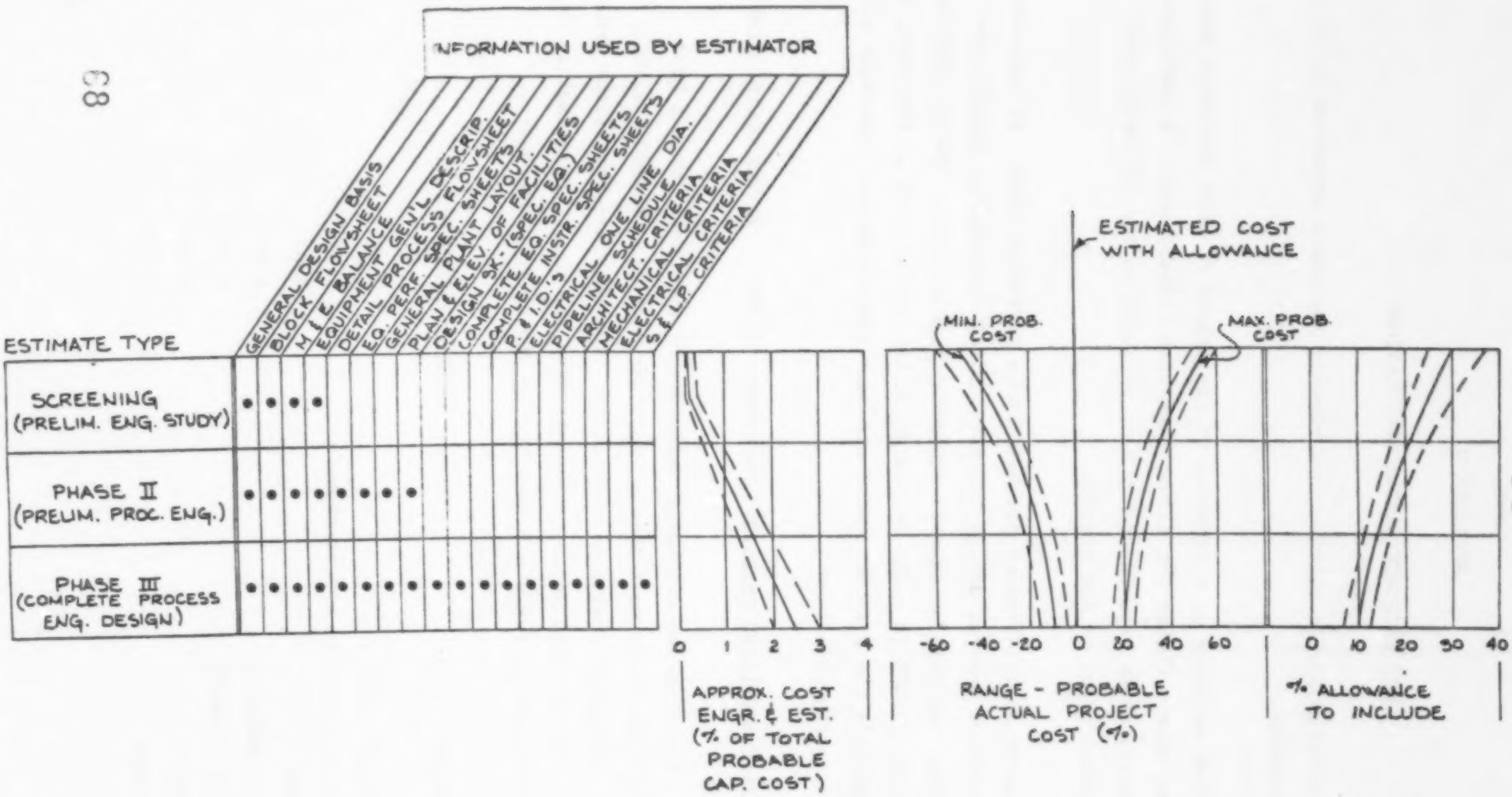

Fig. D-1. Precision of Capital Cost Estimates

Appendix B of Control Device Evaluation. Thermal Oxidizer Supplement (VOC Containing Halogens and Sulfur)[1] was used to estimate the costs as follows. On p B-7 are costs for thermal oxidizers with a residence time of 0.75 sec and with heat recovery operating at 2200°F on off-gas with a heat content of 50 Btu/scf. Since the costs are given for 5,000 and 20,000 scfm, it is necessary to estimate the costs for 8900 scfm by interpolation. This was done by plotting the costs versus the scfm on log-log graph paper and reading the costs for 8900 scfm from the curve:

Total installed capital cost = \$2,700,000
Fixed costs = 780,000/yr
Operating costs = 3,300,000/yr
Gross annual operating cost = 780,000/yr + 3,300,000/yr = \$4,080,000/yr
Recovery credit = 1,100,000/yr
Net annual cost = 4,080,000/yr - 1,100,000/yr = \$2,980,000/yr
From Table VI-1 of this report:
Emission reduction = 1290 + 430 + 1200 = 2900 Mg of EDC/yr

$$\text{Cost effectiveness} = \frac{\$2,980,000/\text{yr}}{2,900 \text{ Mg of EDC/yr}} = \$1,028/\text{Mg of EDC}$$

B. THERMAL OXIDIZER CONTROLLING EMISSIONS FROM MODEL PLANT USING THE OXYCHLORINATION WITH OXYGEN PROCESS

This example is based on the estimated emissions of 1026 scfm, with a heat content of 573 Btu/scf going to a thermal oxidizer operated at 2200°F with a residence time of 0.75 sec and equipped with heat recovery. The estimated emissions include the vent gases from the oxychlorination vent, from the direct-chlorination vent, and from the distillation vents and have the following compositions:

---

[1] H. S. Basdekis, IT Enviroscience, Inc., Control Device Evaluation. Thermal Oxidation Supplement (VOC Containing Halogens or Sulfur) (in preparation for EPA, ESED, Research Triangle Park, NC).

Component	Composition (mole %)
EDC	2.69
Ethylene	20.84
Other chlorinated hydrocarbons	9.52
Ethane	0.58
Carbon monoxide	8.20
Carbon dioxide	21.18
Oxygen	5.09
Nitrogen	31.90

A heat-and-mass balance calculation using an IT Enviroscienc, Inc., computer program shows that no auxiliary fuel is required because of the high heat content. For a temperature of 2200°F, 9770 scfm of combustion air is required, and the flue gases contain over 9 mole % oxygen. The total flow of vent gases and combustion air is 1026 scfm + 9770 scfm = 10,796 scfm.

Two thermal oxidizers operating at 2200°F and 0.75 sec will be the same size and therefore the installed cost will be the same if the flow of flue gas is the same. If it is assumed that the change in scfm due to combustion is either the same or else negligible for both thermal oxidizers, then they will have approximately the same total scfm of entering waste gas, combustion air, and auxiliary fuel, if any. Therefore the costs for a thermal oxidizer sized to handle 1026 scfm of waste gas having a heat content of 573 Btu/scf can be determined by a calculation of the flow of waste gas having a heat content of 100 Btu/scf that will require the same size of thermal oxidizer.

From Fig. III-2 of the thermal oxidation supplement report[1] waste gas with a heat content of 100 Btu/scf will require 24 Btu/scf of waste gas for a combustion temperature of 2200°F. If natural gas with a heat content of 1000 Btu/scf is used, then 0.024 scf of fuel gas per scf of waste gas is required. From Table III-2 of the same report[1] 1.4 scf of combustion air is required per scf of waste gas having a heat content of 100 Btu/scf to give a combustion temperature of 2200°F. The total flow to the thermal oxidizer of waste gas, combustion air, and fuel gas is 1 scf + 1.4 scf + 0.024 scg = 2.424 scf,

$\frac{10{,}796 \text{ scfm}}{2.424 \text{ scf/scf}}$ = 4500 scfm of waste gas (100 Btu/scf).

Therefore the costs for a thermal oxidizer sized to burn 4500 scfm of a 100-Btu/scf waste gas at 2200°F for 0.75 sec are the same as those for a thermal oxidizer that will burn 1026 scfm of a 573-Btu/scf waste gas at the same conditions. On p B-8 of Appendix B of the thermal oxidation supplement report[1] the costs are given for 700 and 5,000 scfm; so interpolation as described above is required to obtain the following:

Total installed capital cost = $1,750,000
Fixed costs = 510,000/yr
Operating costs = 2,450,000/yr
Gross annual operating costs = 510,000 + 2,450,000/yr = $2,960,000/yr
Recovery credit = 560,000/yr
Net annual cost = 2,960,000/yr - 560,000/yr = $2,400,000/yr
From Table VI-1 of this report:
Emission reduction = 185 + 430 + 1200 = 1,800 Mg of EDC/yr
Cost effectiveness = $\frac{\$2{,}400{,}000\text{/yr}}{1{,}800 \text{ Mg of EDC/yr}}$ = $1,333/Mg of EDC

APPENDIX E

LIST OF EPA INFORMATION SOURCES

1. W. M. Reiter, Allied Chemical Corporation, letter to EPA with information on Baton Rouge North Works, May 16, 1978.

2. J. A. DeBernardi, Conoco Chemicals, letter to EPA with information on VCM plant in Lake Charles, Louisiana, May 16, 1978.

3. K. D. Konter, B. F. Goodrich Chemical Company, letter to EPA with information on EDC manufacturing at Calvert City, Kentucky, June 15, 1978.

4. J. A. Mullins, Shell Oil Company, letter to EPA with information on Deer Park, TX, EDC plant, June 22, 1978.

5. R. E. Van Ingen, Shell Oil Company, letter to EPA with information on Deer Park, TX, EDC oxychlorination process, Apr. 10, 1975.

6. R. J. Samelson, PPG Industries, Inc., letter to EPA with information on EDC emissions at Lake Charles, Louisiana, June 2, 1978.

7. F. C. Dehn, PPG Industries, Inc., letter to EPA with information on EDC oxychlorination process, at Lake Charles, Louisiana and at Guayanilla, Puerto Rico, Apr. 15, 1975.

8. W. R. Taylor, Diamond Shamrock Corporation, letter to EPA with information on catalytic oxidation of the oxychlorination vent, at Deer Park, Texas, Oct. 3, 1977 (nonconfidential portion only).

9. W. M. Reiter, Allied Chemical Corporation, letters to EPA with information on EDC oxychlorination process, at Baton Rouge, Louisiana, Apr. 18, 1975, and June 18, 1975.

10. P. B. Cornell, *Louisiana Air Control Commission Emission Inventory Questionnaire for Allied Chemical Corporation North Works, Baton Rouge, LA* (nd).

11. R. M. Teets, Sr., *EPA Questionnaire for Allied Chemical Corporation*, Baton Rouge, Louisiana, Oct. 18, 1972.

12. J. S. Bellecci, *Louisiana Air Control Commission Emission Inventory Questionnaire for Borden Chemical*, Apr. 16, 1975.

13. J. A. DeBernardi, Conoco Chemicals, letters to EPA with information on oxychlorination process, in Lake Charles, Louisiana, Apr. 14, 1975, and Nov. 21, 1974.

14. J. A. DeBernardi, *Louisiana Air Control Commission Emission Inventory Questionnaire for Conoco Chemicals*, May 31, 1961.

15. D. O. Popovac, *EPA Questionnaire for Conoco Chemicals Lake Charles, Louisiana, VCM Plant*, Sept. 1, 1972.

16. Texas Air Control Board, *A Construction Permit···to Diamond Shamrock Chemical Company Authorizing Construction of Vinyl Chloride Plant...at La Porte, Harris County, Texas*, Permit No. C-3855 (Nov. 2, 1976).

17. W. C. Hutton, Texas Air Control Board Emissions Inventory Questionnaire for Diamond Shamrock Corporation, Sept. 15, 1972, and Dec. 29, 1972.

18. R. D. Hall, EPA Questionnaires for Diamond Shamrock Corporation, Sept. 15, 1972, and Dec. 29, 1972.

19. H. W. Johnson, Jr., Texas Air Control Board Emissions Inventory Questionnaires for Dow Chemical Co., Texas Division, Feb. 6, 1976.

20. M. H. Siemens, Dow Chemical USA, letters to EPA with information on oxychlorination vent, at Oyster Creek Division, Nov. 14, 1974, and Feb. 25, 1975 (nonconfidential portions only).

21. M. H. Siemens, Texas Air Control Board 1975 Emissions Inventory Questionnaire for Dow Chemical USA, Oyster Creek Division, Mar. 19, 1976.

22. C. A. Christian, EPA Questionnaire for Dow Chemical USA, Oyster Creek Division, Aug. 4, 1972.

23. G. W. Daigre, EPA Questionnaire for Dow Chemical USA Louisiana Division, Sept. 8, 1972.

24. R. H. Marshall, Texas Air Control Board 1975 Emissions Inventory Questionnaire for Ethyl Corp., Pasadena, Texas, Mar. 21, 1976.

25. J. H. Huguet, EPA Questionnaires for Ethyl Corporation, Baton Rouge, Louisiana, Sept. 8, 1972, and Oct. 19, 1972.

26. W. C. Holbrook, B. F. Goodrich Chemical Company, letter to EPA with information on oxychlorination process at Calvert City, Kentucky, Apr. 7, 1975.

27. C. L. Woods, EPA Questionnaire for B. F. Goodrich Chemical Company Calvert City, Kentucky, June 26, 1972.

28. A. T. Raetzsch, Louisiana Air Control Commission Emission Inventory Questionnaire for PPG Industries, Inc., Mar. 3, 1976.

29. W. B. Graybill and C. A. Burns, EPA Questionnaires for PPG Industries, Inc., Lake Charles, Louisiana, January 1973 and August 1972.

30. R. E. Van Ingen, Shell Oil Company, letters to EPA with information on oxychlorination and direct chlorination vents at Deer Park, Texas, June 14, 1974, July 5, 1974, and Dec. 6, 1974.

31. R. J. Trautner, Louisiana Air Control Commission Emission Inventory Questionnaire for Shell Chemical Company-Norco Plant, Jan. 31, 1977.

32. R. Gliuard, Texas Air Control Board 1975 Emissions Inventory Questionnaire for Shell Chemical Co. Deer Park Manufacturing Complex, Mar. 19, 1976.

33. A. L. de Vries, EPA Questionnaire for Stuaffer Chemical Company Long Beach, California, Jan. 10, 1973.

34. B. G. Perry, Louisiana Air Control Commission Emission Inventory Questionnaire for Union Carbide Corporation Taft Plant, Mar. 6, 1975.

35. R. E. O'Bryan, Texas Air Control Board 1975 Emissions Inventory Questionnaire for Union Carbide Corporation Texas City Plant, Mar. 19, 1976.

36. D. E. Gilbert, Vulcan Materials Company, letter to EPA with information on oxychlorination process at Geismar, Louisiana, Apr. 23, 1974.

37. G. A. Vlacos, Louisiana Air Control Commission Emission Inventory Questionnaire for Vulcan Materials Company Geismar, Louisiana Plant, Aug. 16, 1976.

38. W. W. Duke, EPA Questionnaire for Vulcan Materials Company Geismar, Louisiana Plant, Oct. 12, 1972.

APPENDIX F

EXISTING PLANT CONSIDERATIONS

A. PROCESS CONTROL DEVICES

Table F-1 lists process control devices reported in use by industry. To gather information for the preparation of this report two site visits were made to producers of ethylene dichloride. Trip reports have been cleared by the companies concerned and are on file at EPA, ESED, Research Triangle Park, NC.[1,2] Other sources of the information in this appendix are letters in response to requests by EPA for information on emissions from ethylene dichloride and vinyl chloride plants; see Appendix E. Some were part of the Houdry studies[3—5] or EPA studies of vinyl chloride emissions[6] and were furnished by EPA for use in this study. Some information on existing controls were obtained from the nonconfidential portions of Texas and Louisiana Emission Inventory Questionnaires collected during this study. These are also listed in Appendix E. When information from more than one source did not agree, the data from the source with the latest date was used.

Table F-2[7—14] gives the reported analyses of the emissions from several oxychlorination vents, and Table F-3 gives the reported analyses from three direct-chlorination vents. Similar data are in the Houdry reports[3—5] and supporting letters (see Appendix E) and were also used in preparing this report.

B. RETROFITTING CONTROLS

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of the costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant.

No thermal oxidizers have been retrofitted to air process oxychlorination vents;[3] however, Borden's recently constructed plant at Geismar has a thermal oxidizer with heat recovery that is fed the vent gases from their oxychlorination (air) step and several other vent gas streams. When visited, their unit had been out of service for modifications to correct design problems and so no actual operating data are yet available.[1]

Table F-1. Emission Controls Used by the Ethylene Dichloride Industry[a]

Company and Location	Process Used	Date of Construction	Emission Sources	VOC Emission Rate	Control Technique or Device Used
Allied					
Baton Rouge, LA	Air	NR[b]	Oxychlorination vent	1390 kg/hr	None
			Stripper ejector	98 lb/hr[c]	None
			Purification vent	230 lb/hr[c]	Return to process
Borden					
Geismar, LA	Air	1977	Oxychlorination vent	NR	Thermal oxidizer
			Direct-chlorination vent	NR	Thermal oxidizer
			Purification vents	NR	Thermal oxidizer
Conoco					
Westlake, LA	Air	NR	Oxychlorination vent	1085 lb/hr	Post reactor
			Direct-chlorination vent	69 lb/hr	Refrigerated condenser[d]
			Purification vents	NR	Water scrubber
Diamond Shamrock					
Deer Park, TX	Air	NR	Oxychlorination vent	260 lb/hr	Catalytic oxidizer
			Direct-chlorination vent	NR	Refrigerated condenser
			Purification vents	NR	Vent condensers
La Porte, TX	Air	1978	Process vents	NR	Thermal oxidizer
Dow					
Freeport, TX	NR	NR	Process vents	NR	Thermal oxidizer
Oxyster Creek, TX	Oxygen	1968	Process vents	NR	Thermal oxidizer
B. F. Goodrich					
Calvert City, KY	Air	NR	Oxychlorination vent	1880 lb/hr	Solvent absorption
			Direct-chlorination vent	119 lb/hr	Refrigerated vent condenser

Table F-1. (Continued)

Company and Location	Process Used	Date of Construction	Emission Sources	VOC Emission Rate	Control Technique or Device Used
PPG					
Lake Charles, LA	Oxygen	1969	Oxychlorination vent	570 lb/hr	Thermal oxidizer
			Direct-chlorination vent	700 lb/hr	Thermal oxidizer
Guayanilla, PR	Oxygen	NR	Process vents	NR	Thermal oxidizer
Shell					
Deer Park, TX	Air	NR	Oxychlorination vent	1040 lb/hr	Post reactor
			Direct-chlorination vent	495 lb/hr	Thermal oxidizer
			Purification vents		
			Storage vents		
Vulcan					
Geismar, LA	Air	NR	Oxychlorination vent	250 lb/hr	Chilled water scrubber
			Purification vents	100 lb/hr	None

[a] See Appendix E.

[b] Not reported.

[c] Design data.

[d] Plans to install a thermal oxidizer.

Table F-2. Reported Uncontrolled Emissions from Oxychlorination Vents

Component	Compositions Reported by Allied[a] (wt %)	Conoco[b] (lb/hr)	Diamond Shamrock[c] (lb/hr)	B. F. Goodrich[d] (lb/hr)	PPG[e] (wt %)	Shell[f] (wt %)	Vulcan[g] (lb/hr)
EDC	3.03	414	74.4	200		0.75	130
Ethyl chloride	0.92	489				1.00	0.59
Ethylene		117	183.1	318	26	0.02	119
Other VOC	6.53	60	2.45	68	3	0.23	0.75
Ethane	0.92	5		106			254
Methane	0.9	42		647			
Carbon dioxide	2.13	895		2,045	44		
Carbon monoxide	0.86	434	243.5	481	4	1.00	119
Nitrogen	79.25	42,227		62,688	15		
Oxygen	5.44		1,270	5,076	3		
Total			18,900				

[a] See refs 7 and 8.

[b] See ref 9.

[c] See ref 10.

[d] See ref 11.

[e] See ref 12.

[f] See ref 13.

[g] See ref 14.

Table F-3. Reported Uncontrolled Emissions from Direct-Chlorination Vents

	Compositions Reported by		
Component	Conoco[a] (mole %)	PPG[b] (wt %)	Shell[c] (wt %)
EDC	1.7	5	4.6
Ethyl chloride	0.01	5	2.1
Ethylene	3.3	44	0.8
Other VOC	0.02		2.6
Ethane	0.8	2	
Methane	15.1		
Carbon dioxide	1.63	19	
Carbon monoxide	1.1		1.2
Nitrogen	42.8	17	
Oxygen	14.5		
Hydrogen	4.4		

[a] See ref 9.

[b] See ref 12.

[c] Includes vents on reactor, wash system, purification, storage, and steam stripper; see ref 13.

Diamond Shamrock has retrofitted a commercial-sized catalytic oxidizer to their older oxychlorination facility. The unit reportedly does remove carbon monoxide and ethylene with better than 99.7% reduction; however, it removes less than 75% of the ethylene dichloride and less than 60% of the VCM, with 100 ppm of ethylene dichloride and 8 ppm of VCM remaining in the stack gases.[10]

Because some companies may have excess steam capacity on-site, it may not be economically feasible to retrofit a thermal oxidizer with heat recovery. Both PPG and Dow have indicated plans to incorporate heat recovery in their thermal oxidizers.[15,16]

C. REFERENCES*

1. J. A. Key, IT Enviroscience, Inc., Trip Report for Visit to Borden Chemical, Geismar, LA, Mar. 2, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

2. J. A. Key, IT Enviroscience, Inc., Trip Report for Visit to Dow Chemical, U.S.A., Oyster Creek Division, Freeport, TX, Sept. 20, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

3. R. G. Bellamy and W. A. Schwartz, Houdry Div., Air Products and Chemicals, Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry. Volume 8: Vinyl Chloride Manufacture by the Balanced Process, EPA-450/3-73-006-h, Research Triangle Park, NC (July 1975).

4. W. A. Schwartz et al., Houdry Div., Air Products and Chemicals, Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry. Volume 3: Ethylene Dichloride Manufacture by Oxychlorination, EPA-450/3-73-006-c, Research Triangle Park, NC (April 1974).

5. J. W. Pervier et al., Houdry Div., Air Products and Chemicals, Survey Reports on Atmospheric Emissions from the Petrochemical Industry, vol II, EPA-450/3-73-005-b, Research Triangle Park, NC (April 1974).

6. Standard Support and Environmental Impact Statement: Emission Standard for Vinyl Chloride, EPA-450/2-75-009, Research Triangle Park, NC (October 1975).

7. W. M. Reiter, Allied Chemical Corporation, letter to EPA with information on Baton Rouge North Works, May 16, 1978.

8. Personal communication between B. A. Boeneke, Allied Chemical Corporation, Baton Rouge, LA, and D. C. Mascone, EPA, Aug. 21, 1978.

9. J. A. DeBernardi, Conoco Chemicals, letter to EPA with information on VCM plant in Lake Charles, LA, May 16, 1978.

10. W. R. Taylor, Diamond Shamrock Corporation, letter to EPA with information on catalytic oxidation of the oxychlorination vent at Deer Park, TX, Oct. 3, 1977 (nonconfidential portion only).

11. W. C. Holbrook, B. F. Goodrich Chemical Company, letter to EPA with information on oxychlorination process at Calvert City, KY, Apr. 7, 1975.

12. R. J. Samelson, PPG Industries, Inc., letter to EPA with information on EDC emissions at Lake Charles, LA, June 2, 1978.

13. J. A. Mullins, Shell Oil Company, letter to EPA with information on Deer Park, TX, EDC plant, June 22, 1978.

14. C. V. Gordon, Vulcan Materials Company, letter to EPA with information on EDC plant at Geismar, LA, Oct. 24, 1978.

15. M. H. Siemens, Dow Chemical USA, letters to EPA with information on oxychlorination vent at Oyster Creek Division, Nov. 14, 1974, and Feb. 25, 1975 (nonconfidential portions only).

16. F. C. Dehn, PPG Industries, Inc., letter to EPA with information on EDC oxychlorination process at Lake Charles, LA, and at Guayanilla, PR, Apr. 15, 1975.

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

REPORT 2

CARBON TETRACHLORIDE AND PERCHLOROETHYLENE BY THE HYDROCARBON CHLORINOLYSIS PROCESS

(ABBREVIATED REPORT)

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Research Triangle Park, North Carolina

September 1980

This report contains certain information which has been extracted from the Chemical Economics Handbook, Stanford Research Institute. Wherever used, it has been so noted. The proprietary data rights which reside with Stanford Research Institute must be recognized with any use of this material.

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1×10^{12} grams
G	giga	10^{9}	1 Gg = 1×10^{9} grams
M	mega	10^{6}	1 Mg = 1×10^{6} grams
k	kilo	10^{3}	1 km = 1×10^{3} meters
m	milli	10^{-3}	1 mV = 1×10^{-3} volt
μ	micro	10^{-6}	1 μg = 1×10^{-6} gram

II. INDUSTRY DESCRIPTION

A. INTRODUCTION

There are several processes by which chloromethanes are produced either as co-products or individually. One process also results in the production of perchloroethylene as a co-product. A previous product report[1] describes the processes of methanol hydrochlorination to produce methyl chloride and of methyl chloride chlorination to produce methylene chloride, chloroform, and by-product carbon tetrachloride. Another product report[2] describes the process of methane chlorination to produce methyl chloride, methylene chloride, chloroform, and carbon tetrachloride. The process of carbon disulfide chlorination to produce carbon tetrachloride will not be reported in detail because of the decline in carbon tetrachloride usage and the subsequent decline in the importance of the carbon disulfide chlorination process. The process of hydrocarbon chlorinolysis to produce carbon tetrachloride and perchloroethylene as co-products is described in this report.

B. CARBON TETRACHLORIDE

1. General Description

Carbon tetrachloride is a heavy, volatile liquid at ambient conditions (see Appendix A for pertinent physical properties). It is produced by chlorinolysis of mixed hydrocarbons, methane chlorination, or carbon disulfide chlorination. Emissions of VOC (volatile organic compounds) resulting from carbon tetrachloride manufacture include carbon tetrachloride and perchloroethylene from the chlorinolysis of mixed hydrocarbons process, all the chloromethanes from the methane chlorination process, and carbon tetrachloride and carbon disulfide from the carbon disulfide chlorination process.[1,2]

2. Usage and Growth

Table II-1 (ref. 3) gives the end uses of carbon tetrachloride. About 90% of carbon tetrachloride consumption in recent years has been as an intermediate in the production of trichlorofluoromethane and dichlorodifluoromethane. These two compounds have been the subject of much controversy concerning their potential contribution to the depletion of stratospheric ozone. The result has been a 27% drop in consumption of carbon tetrachloride between 1974 and 1976.[4] (The EPA promulgated regulations controlling fully halogenated chlorofluoroalkanes on

Table II-1. Carbon Tetrachloride Usage[a,b]

End Use	1977 Production (%)
Trichlorofluoromethane	33.8
Dichlorodifluoromethane	55.0
Miscellaneous	11.2

[a] See ref 3.

[b] Data on growth rates not available.

March 17, 1978.[5]) The current domestic carbon tetrachloride production capacity is about 555,000 Mg/yr, with 1979 production[4] utilizing only about 57% of that capacity. Production is expected to decline by as much as 10% annually.[6] There are no known plans to increase carbon tetrachloride capacity.

3. Domestic Producers

In 1979 six domestic producers of carbon tetrachloride were operating eleven plants. Table II-2 lists the producers, locations, capacities, and manufacturing processes; Fig. II-1 shows the plant locations. Dow at Freeport, TX, Pittsburg, CA, and Plaquemine, LA; Stauffer at Louisville, KY; and Vulcan at Geismar, LA, and Wichita, KS, all operate plants based on chlorinolysis (see Sect. III-A) of mixed hydrocarbon feed streams and produce perchloroethylene as a co-product. Allied; Dow at Freeport, TX, and Pittsburg, CA; FMC; Stauffer at Louisville, KY; and Vulcan at Wichita, KS, are reported[4] to operate plants using the methane chlorination process, which produces carbon tetrachloride as one of the co-products. Some of these producers may be using methane feed in the chlorinolysis process. Stauffer at LeMoyne, AL, and Niagara Falls, NY, operates carbon tetrachloride production plants that use the carbon disulfide chlorination process. FMC operated a carbon disulfide chlorination process at South Charleston, WV, which was shut down in 1979. No information on capacity or raw material is available on the Inland Chemical Corporation plant at Manati, PR. Capacities for all plants other than those using the carbon disulfide chlorination process are flexible since reaction conditions can be adjusted to vary the yields of carbon tetrachloride and its co-products.

C. PERCHLOROETHYLENE

1. General Description

Perchloroethylene is a heavy liquid with moderate volatility at ambient conditions (see Appendix A for pertinent physical properties). It is produced by chlorination of ethylene dichloride or acetylene and by the chlorinolysis process, which produces carbon tetrachloride as a co-product. Emissions from its production include perchloroethylene and co-products, as well as feed materials, depending on the manufacturing process.

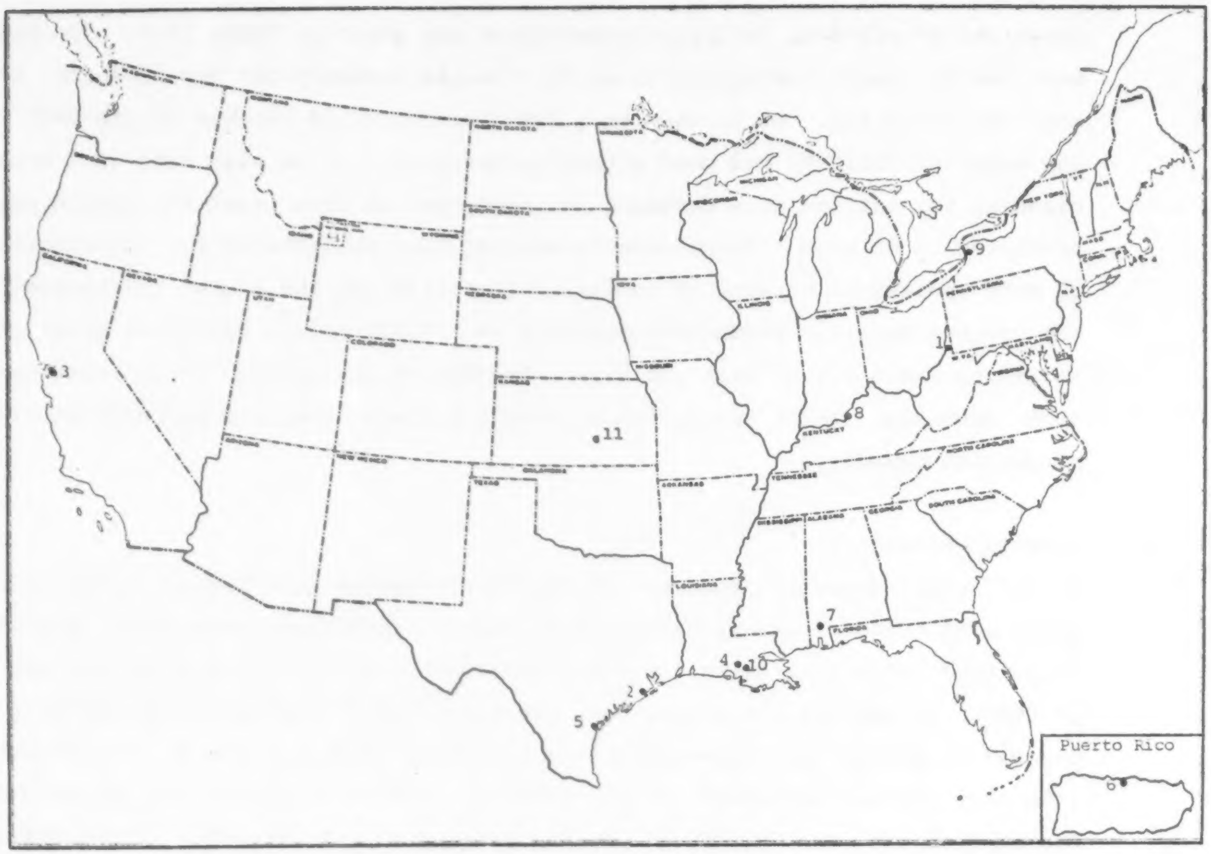
Table II-2. Carbon Tetrachloride Capacity[a]

Plant	1977 Capacity[b] (X 10^3 Mg)	Process
Allied, Moundsville, WV	4	Methyl chloride chlorination and methane chlorination
Dow, Freeport, TX	61	Methane chlorination and chlorinolysis of mixed hydrocarbon feed with perchloroethylene co-product
Dow, Pittsburg, CA	36	Methane chlorination and chlorinolysis of mixed hydrocarbon feed with perchloroethylene co-product
Dow, Plaquemine, LA	57	Chlorinolysis of mixed hydrocarbon feed with perchloroethylene co-product
Du Pont, Corpus Christi, TX	154	
Inland, Manati, PR	c	c
Stauffer, Le Moyne, AL	91	Carbon disulfide chlorination
Stauffer, Louisville, KY	16	Methane chlorination and chlorinolysis of mixed hydrocarbon feed with perchloroethylene co-product
Stauffer, Niagara Falls, NY	68	Carbon disulfide chlorination
Vulcan, Geismar, LA	41	Chlorinolysis of mixed hydrocarbon feed with perchloroethylene co-product
Vulcan, Wichita, KS	27	Methyl chloride chlorination, methane chlorination, and chlorinolysis of mixed hydrocarbon feed with perchloroethylene co-product
Total	555	

[a] See ref 4.

[b] Production ratios are very flexible, especially when co-products are involved.

[c] Not available.



(1) Allied Chemical Corp., Moundsville, WV
(2) Dow Chemical Co., Freeport, TX
(3) Dow Chemical Co., Pittsburg, CA
(4) Dow Chemical Co., Plaquemine, LA
(5) Du Pont, Corpus Christi, TX
(6) Inland Chemical Corp., Manti, PR
(7) Stauffer Chemical Co., Le Moyne, AL
(8) Stauffer Chemical Co., Louisville, KY
(9) Stauffer Chemical Co., Niagara Falls, NY
(10) Vulcan Materials Co., Geismar, LA
(11) Vulcan Materials Co., Wichita, KS

Fig. II-1. Locations of Plants Manufacturing Carbon Tetrachloride

2. Usage and Growth

Usage and growth data for perchloroethylene are given in Table II-3. The predominant use of perchloroethylene is in the textile industry for dry cleaning, processing, and finishing. It is used as a dry-cleaning fluid because of its high density, low water solubility, and good solvent properties. It is also used as a metal cleaning solvent and as a chemical intermediate; in both cases the growth rate is predicted to be high. Perchloroethylene has been substituted for trichloroethylene in many operations because of regulations restricting the use of trichloroethylene.[7] The current domestic production capacity is 575,000 Mg/yr, with 1979 production[8] utilizing about 56% of that capacity. Production is expected to increase by about 5.5%[7] annually. There are no known immediate plans to expand perchloroethylene production capacity.

3. Domestic Producers

In 1977 eight domestic producers of perchloroethylene were operating eleven plants. Table II-4 (refs. 7 and 9) lists the producers, locations, capacities, and processes used; Fig. II-2 shows the plant locations. Three of the producers are reported[7,9] to operate six plants that use the mixed hydrocarbon chlorinolysis process to produce perchloroethylene with carbon tetrachloride as a co-product (the only process pertinent to this report). The seven plants are operated by Dow at Freeport, TX, Pittsburg, CA, and Plaquemine, LA; Stauffer at Louisville, KY; and Vulcan at Geismar, LA, and Wichita, KS.

Table II-3. Perchloroethylene Usage and Growth*

End Use	1974 Production (%)	Average Annual Growth (%) for 1974—1979
Textile industry (dry cleaning, processing, finishing)	69	4
Metal cleaning solvent	16	11
Chemical intermediate	12	7
Miscellaneous	3	2

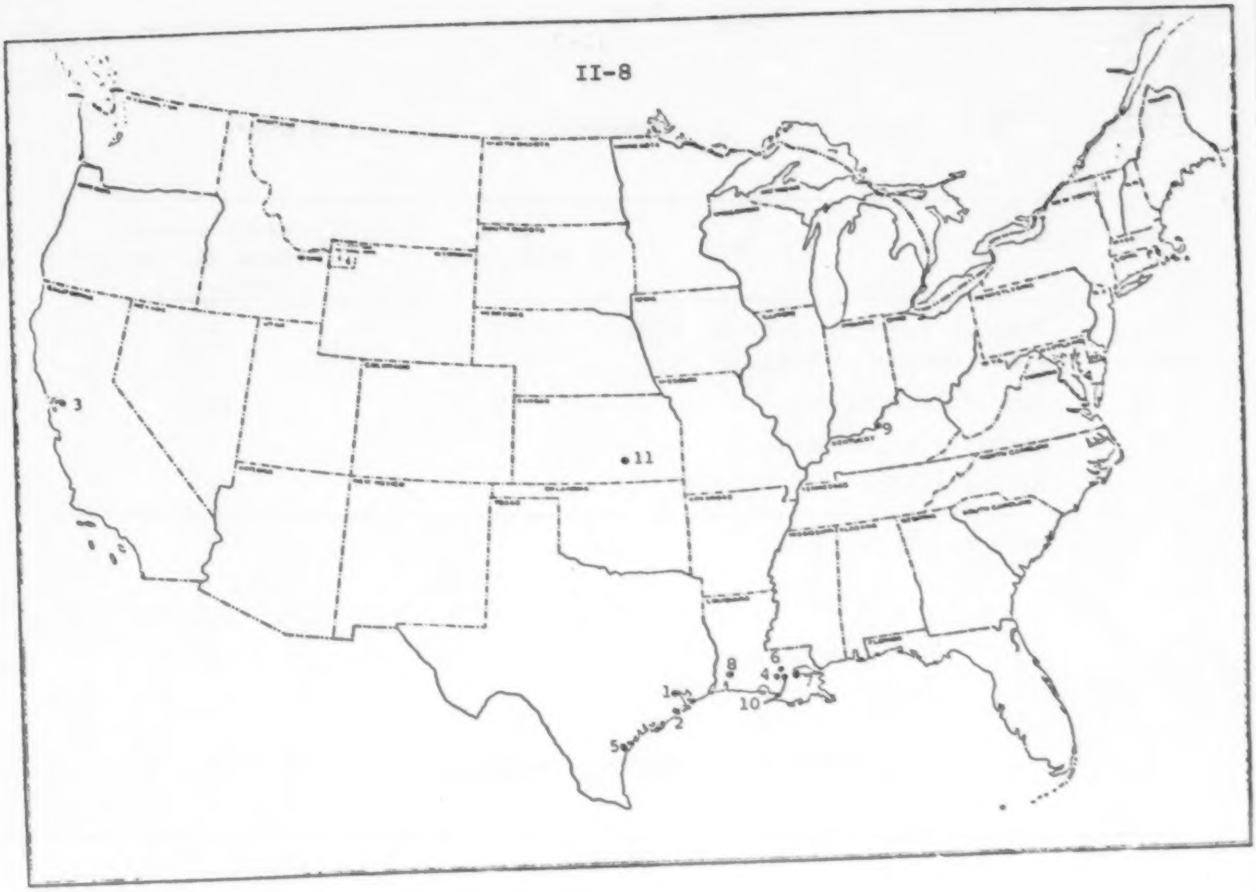
*See ref 7.

Table II-4. Perchloroethylene Capacity[a]

Plant	1977 Capacity (X 10^3 Mg)[b]	Process
Diamond Shamrock, Deer Park, TX	75	Ethylene dichloride chlorination
Dow, Freeport, TX	54	Chlorinolysis of mixed hydrocarbons producing carbon tetrachloride as a co-product
Dow, Pittsburg, CA	9	Same as above
Dow, Plaquemine, LA	68	Same as above
Du Pont, Corpus Christi, TX	73	
Ethyl, Baton Rouge, LA	45	Ethylene dichloride chlorination
Hooker, Taft, LA	27	Acetylene chlorination
PPG, Lake Charles, LA	109	Ethylene dichloride chlorination
Stauffer, Louisville, KY	32	Chlorinolysis of mixed hydrocarbons producing carbon tetrachloride as a co-product
Vulcan, Geismar, LA	60	Same as above
Vulcan, Wichita, KS	23	Same as above
Total	575	

[a] See refs 7 and 9.

[b] Capacities can vary from the listed amounts because other chlorinated compounds can be manufactured with the same equipment.



(1) Diamond Shamrock Corp., Deer Park, TX
(2) Dow Chemical Co., Freeport, TX
(3) Dow Chemical Co., Pittsburg, CA
(4) Dow Chemical Co., Plaquemine, LA
(5) Du Pont, Corpus Christi, TX.
(6) Ethyl Corp., Baton Rouge, LA
(7) Hooker Chemical Corp., Taft, LA
(8) PPG Industries, Inc., Lake Charles, LA
(9) Stauffer Chemical Co., Louisville, KY
(10) Vulcan Materials Co., Geismar, LA
(11) Vulcan Materials Co., Wichita, KS

Fig. II-2. Locations of Plants Manufacturing Perchloroethylene

D. REFERENCES*

1. F. D. Hobbs and C. W. Stuewe, IT Enviroscience, Inc., Chloromethanes. Methanol Hydrochlorination and Methyl Chloride Chlorination Processes (in preparation for EPA, ESED, Research Triangle Park, NC).

2. F. D. Hobbs and C. W. Stuewe, IT Enviroscience, Inc., Chloromethanes. Methane Chlorination Process (in preparation for EPA, ESED, Research Triangle Park, NC).

3. "(635.2030M) Chlorinated Methanes——Salient Statistics," p 235 in Chemical Economics Handbook, Manual of Current Indicators——Supplemental Data, Chemical Information Services, Stanford Research Institute, Menlo Park, CA (June 1980).

4. E. M. Klapproth, "Carbon Tetrachloride——Salient Statistics," pp. 635.2030A-E in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (April 1976).

5. Environmental Protection Agency, "Fully Halogenated Chlorofluoroalkanes," Federal Register, Vol. 43, Part II, p. 11318 (Mar. 17, 1978).

6. "Chemical Profile on Carbon Tetrachloride," p. 9 in Chemical Marketing Reporter (Oct. 1, 1975).

7. J. L. Blackford, "Perchloroethylene," pp. 685.5031A—685.5033A in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (November 1975).

8. "(632.3001J) C_2 Chlorinated Solvents," p 228 in Chemical Economics Handbook, Manual of Current Indicators——Supplemental Data, Chemical Information Services, Stanford Research Institute, Menlo Park, CA (June 1980).

9. "Chemical Profile on Perchloroethylene," p. 9 in Chemical Marketing Reporter (Aug. 9, 1976).

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTION

A. INTRODUCTION

Carbon tetrachloride and perchloroethylene coproducts, along with some chlorinated hydrocarbon by-products, are manufactured by chlorination of hydrocarbons at or near pyrolytic conditions in a process commonly referred to as chlorinolysis.[1] The hydrocarbon feed to this process can be any of several hydrocarbons or a mixture of hydrocarbons. The reactions using propane or propylene as feed materials are as follows:

$$\underset{\text{(propane)}}{C_3H_8} + \underset{\text{(chlorine)}}{8Cl_2} \longrightarrow \underset{\substack{\text{(perchloro-}\\\text{ethylene)}}}{C_2Cl_4} + \underset{\substack{\text{(carbon}\\\text{tetrachloride)}}}{CCl_4} + \underset{\substack{\text{(hydrogen}\\\text{chloride)}}}{8HCl}$$

$$\underset{\text{(propylene)}}{C_3H_6} + \underset{\text{(chlorine)}}{7Cl_2} \longrightarrow \underset{\substack{\text{(perchloro-}\\\text{ethylene)}}}{C_2Cl_4} + \underset{\substack{\text{(carbon}\\\text{tetrachloride)}}}{CCl_4} + \underset{\substack{\text{(hydrogen}\\\text{chloride)}}}{6HCl}$$

Also important in the process is the equilibrium established between the coproducts as represented by the equation

$$\underset{\substack{\text{(carbon}\\\text{tetrachloride)}}}{2CCl_4} \rightleftharpoons \underset{\text{(perchloroethylene)}}{C_2Cl_4} + \underset{\text{(chlorine)}}{2Cl_2}$$

As an example of the variety of hydrocarbons that can be used in the process, crude carbon tetrachloride byproduct from the methanol hydrochlorination and methyl chloride chlorination process, as described in a previous report,[2] can be used as feed to the reaction.[3]

B. HYDROCARBON CHLORINOLYSIS PROCESS

The process flow diagram shown in Fig. III-1 represents a typical continuous process for the chlorinolysis of hydrocarbons to produce carbon tetrachloride and perchloroethylene. Preheated hydrocarbon feed material (Stream 1) and chlorine (Stream 2) enter the chlorinolysis reactor, which is a fluid-bed reactor maintained at about 500°C and contains copper and barium chloride on graphite as a catalyst. The addition rate of feed materials is used to control the reactor temperature. With proper

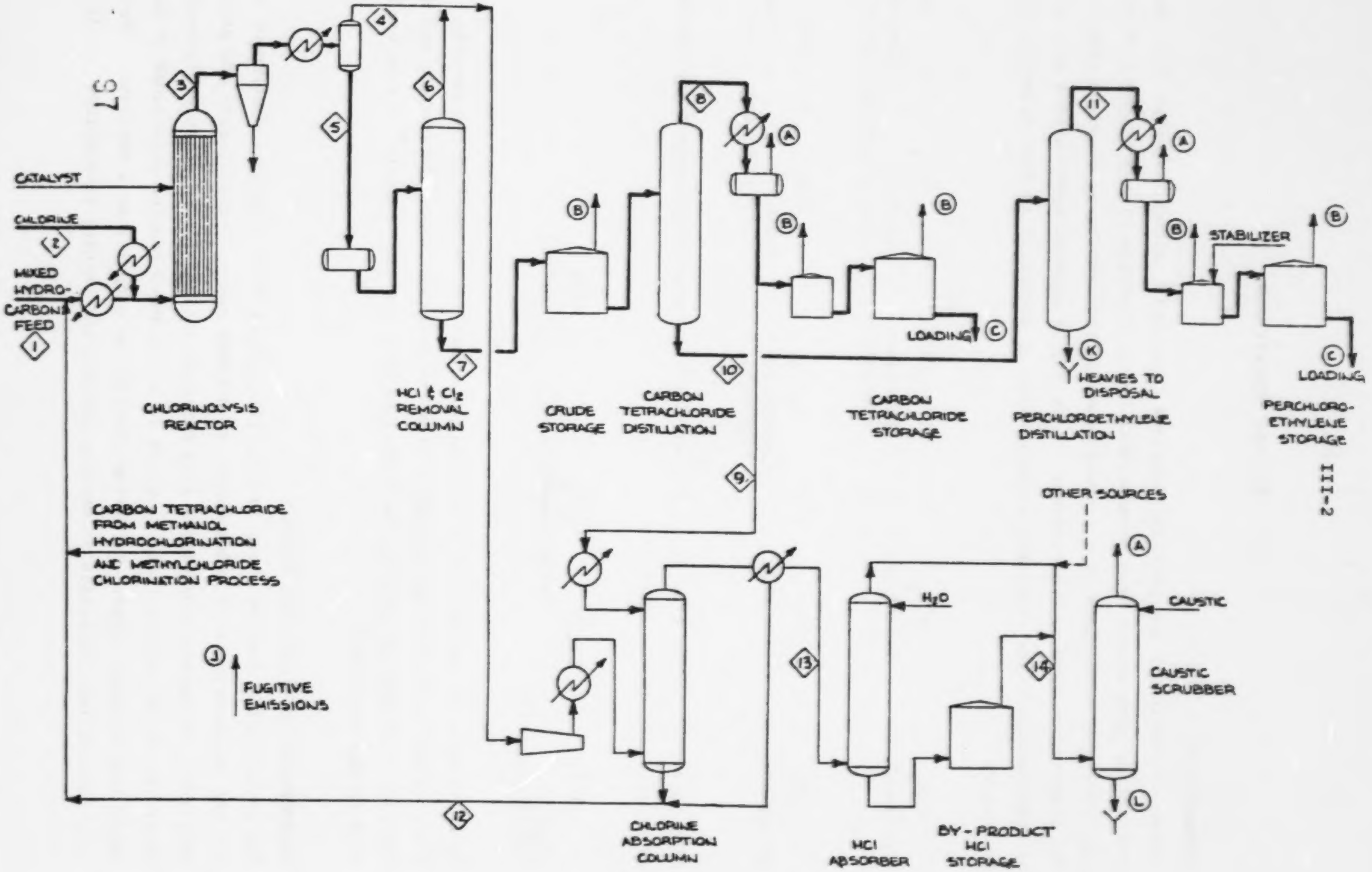

CATALYST
CHLORINE
2
MIXED HYDRO-CARBONS FEED
1
3
4
5
6
7
CHLORINOLYSIS REACTOR
HCl & Cl2 REMOVAL COLUMN
B
CRUDE STORAGE
8
A
10
CARBON TETRACHLORIDE DISTILLATION
B
B
LOADING
C
CARBON TETRACHLORIDE STORAGE
11
A
K
HEAVIES TO DISPOSAL
PERCHLOROETHYLENE DISTILLATION
B
STABILIZER
B
C
LOADING
PERCHLORO-ETHYLENE STORAGE
9
CARBON TETRACHLORIDE FROM METHANOL HYDROCHLORINATION AND METHYLCHLORIDE CHLORINATION PROCESS
J
FUGITIVE EMISSIONS
12
CHLORINE ABSORPTION COLUMN
13
H2O
HCl ABSORBER
BY-PRODUCT HCl STORAGE
OTHER SOURCES
14
A
CAUSTIC
CAUSTIC SCRUBBER
L

Fig. III-1. Process Flow Diagram for Manufacture of Carbon Tetrachloride and Perchloroethylene by Hydrocarbon Chloronolysis

"

control of reaction conditions the chlorine and hydrocarbon feed will be almost completely converted to carbon tetrachloride and perchloroethylene products plus hydrogen chloride and chlorinated hydrocarbon by-products.[4]

The reaction products (Stream 3) pass through a cyclone for removal of entrained catalyst and then on to a condenser. Uncondensed materials (Stream 4), consisting of hydrogen chloride, unreacted chlorine, and some carbon tetrachloride, are removed to the hydrogen chloride purification system. The condensed material (Stream 5) is fed to a hydrogen chloride and chlorine removal column, with the overheads (Stream 6) from this column going to hydrogen chloride purification. The bottoms (Stream 7) from the column are fed to a crude storage tank. Material from crude storage is fed to a carbon tetrachloride distillation column, with the overheads (Stream 8) passing either to carbon tetrachloride storage and loading or to the hydrogen chloride purification system (Stream 9). The bottoms (Stream 10) from the carbon tetrachloride distillation column are fed to a perchloroethylene distillation column. The overheads (Stream 11) from the perchloroethylene distillation column are taken to perchloroethylene storage and loading, and the bottoms are removed for disposal by incineration.

The feed streams (Streams 4 and 6) to hydrogen chloride purification are compressed, cooled, and scrubbed in a chlorine absorption column with chilled carbon tetrachloride (Stream 9) to remove chlorine. The bottoms and condensable overheads (Stream 12) from this column are combined and recycled to the chlorinolysis reactor. Uncondensed overheads (Stream 13) from the chlorine absorption column are water-scrubbed in the hydrogen chloride absorber. Hydrochloric acid solution is removed from the bottom of this absorber to storage for eventual reprocessing or for use in a separate facility. Overheads from the absorber and vented gases from by-product hydrochloric acid storage are combined (Stream 14) and passed through a caustic scrubber for removal of residual hydrogen chloride. Inert gases are vented from the scrubber.

Process emission sources originate at the carbon tetrachloride and perchloroethylene distillation condensers and caustic scrubber (Vents A).

Fugitive emissions throughout the process can contain carbon tetrachloride and perchloroethylene. Corrosion problems caused by chlorine and hydrogen chloride can increase fugitive emissions. Storage and handling emissions (labeled B and C, respectively, on Fig. III-1) include carbon tetrachloride and perchloroethylene.

Two potential sources of secondary emissions result from handling and incineration of bottoms from perchloroethylene distillation (labeled K on Fig. III-1) and from waste caustic from the caustic scrubber (labeled L on Fig. III-1).

C. PROCESS VARIATIONS

There are several possible variations in the process and the manner in which individual steps within the process are operated as described below. Even a variant, however, will require the same process steps as those described for the model process, for example, hydrogen chloride and chlorine removal and recovery and product purification, storage, and loading. Variations in the manner of operation are possible without affecting process emissions.

A broad range of hydrocarbon feeds, catalyst systems, and reaction conditions can be used in the chlorinolysis reactor. Likewise, empty chamber reactors and higher temperatures can be used for chlorinolysis.

Carbon tetrachloride can be injected into the chlorinolysis reactor to shift the equilibrium established between carbon tetrachloride and perchloroethylene to increase the production rate of perchloroethylene.[4] This practice will necessitate changes in subsequent storage requirements and emissions.

Carbon tetrachloride may be caustic-scrubbed to remove traces of hydrogen chloride after carbon tetrachloride distillation, which would require a drying operation. A steam stripper can be used to treat effluent from the caustic scrubbing and drying operations for removal of carbon tetrachloride, which can be recycled.[5]

Additional storage may be required when liquid hydrocarbons are used as feed to the chlorinolysis reactor. Such storage will create emissions that will vary in amounts according to the composition and vapor pressure of the material being stored and the storage conditions. For example, storage of by-product crude carbon tetrachloride (the feed material) from a 90,000-Mg/yr methanol hydrochlorination and methyl chloride chlorination model plant results in calculated emissions of 0.49 kg/hr. This emission source was included in the methanol hydrochlorination and methyl chloride chlorination process described in another product report.[2]

One producer reported[6] several specific process variations which are as follows:

1. Thermal chlorination is used instead of the fluid bed catalytic process.
2. A quench tower following the thermal reactor removes heavy ends from the process. Heavy ends from the perchloroethylene distillation are recycled to the quench tower.
3. A light-ends stripper follows the quench tower. The light ends are recycled to the reactor.
4. Most inerts in the process are separated in the hydrogen chloride absorption and chlorine removal system.
5. Solid-phase neutralizer and dessicant traps are used.
6. The caustic scrubber is used only during startups and emergencies.

D. REFERENCES*

1. D. W. F. Hardie, "Chlorocarbons and Chlorohydrocarbons," p. 132 in Kirk-Othmer Encyclopedia of Chemical Technology, vol. 5, 2d ed., Interscience, New York, 1964.

2. F. D. Hobbs and C. W. Stuewe, IT Enviroscience, Inc., Chloromethanes. Methanol Hydrochlorination and Methyl Chloride Chlorination Process (in preperation for EPA, ESED, Research Triangle Park, NC).

3. F. D. Hobbs, IT Enviroscience, Inc., Trip Report on Visit to Vulcan Materials Co., Geismar, LA, Jan. 4, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

4. L. M. Elkin, Chlorinated Solvents, Report No. 48, A Private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (ND).

5. List of EPA Data Sources (on file at EPA, ESED, Research Triangle Park, NC) (see Appendix C).

6. Thomas A Robinson, Vulcan Materials Company, Wichita, KS, letter dated July 9, 1979, to David R. Patrick, EPA.

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

A. INTRODUCTION

An 80,000-Mg/yr model plant, based on 8760 hr of operation,* was selected to represent today's hydrocarbon chlorinolysis industry; individual product capacities were selected to be 50,000-Mg/yr perchloroethylene and 30,000-Mg/yr carbon tetrachloride. The individual product capacities were selected on the basis of perchloroethylene's expected growth in usage and the declines in demand for carbon tetrachloride. The total capacity was based on an approximate mid-range of today's domestic industry. The model process shown in Fig. III-1 is typical of many plants and best fits today's manufacturing and engineering technology. Single-process trains as shown are typical.

Typical intermediate- and product-storage requirements were estimated for a 50,000-Mg/yr perchloroethylene and a 30,000-Mg/yr carbon tetrachloride plant. Storage tanks for feed materials were not included in the plant design, although producers using liquid waste hydrocarbons, such as the crude carbon tetrachloride by-product described in an earlier report,[1] would require such storage facilities.

B. SOURCES AND EMISSIONS

Emission rates and ratios and sources for the hydrocarbon chlorinolysis process are summarized in Table IV-1.

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*Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will ususally operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations the error introduced by assuming continuous operation is negligible.

Table IV-1. Uncontrolled[a] Emissions from 80,000-Mg/Yr Chlorinolysis Process Plant

Emission Source	Stream Designation (Fig.III-1)	Uncontrolled Emissions Ratio (kg/Mg)[b] Ethylene Dichloride[c]	Uncontrolled Emissions Ratio (kg/Mg)[b] Vinylidene Chloride[c]	Uncontrolled Emissions Ratio (kg/Mg)[b] Total VOC[d]	Uncontrolled Emissions Rate (kg/hr) Ethylene Dichloride[c]	Uncontrolled Emissions Rate (kg/hr) Vinylidene Chloride[c]	Uncontrolled Emissions Rate (kg/hr) Total VOC
Process vents	A			0.0053			0.049
Storage	B			0.52			4.77
Handling	C			0.13			1.2
Fugitive	J			1.48			13.51
Hex waste handling and disposal and waste hydrocarbon storage[e]	K	0.026	0.013	0.056	0.24	0.12	0.51
Waste caustic	L			0.15			1.4
Total		0.026	0.013	2.34	0.24	0.12	21.4

[a] Emissions from plants employing no controls other than those necessary for economical operation.

[b] kg of emission per Mg of product.

[c] Ethylene dichloride and vinylidene chloride are considered by the EPA to be hazardous substances and are reported separately.

[d] Composition of emissions will vary according to the feeds to the process.

[e] This source of emissions includes handling and incineration of the hex waste and the emissions from waste hydrocarbons storage tanks as reported by one producer (see ref. 2). This source is described in detail in Sect. IV-B-4.

1. Process Emissions

Inert gases enter the process with the chlorine and hydrocarbons fed to the chlorinolysis reactor. Vents for the purging of these inert gases from the process are associated with the carbon tetrachloride and perchloroethylene distillation condensers and the caustic scrubber following hydrochloric acid recovery (Vents A, Fig. III-1). Limited information is available concerning the individual vents. One producer reported[2] no emissions from the carbon tetrachloride condenser vent and very limited emissions from the perchloroethylene condenser vent for a calculated total emission ratio from these two sources of less than 1×10^{-5} kg of VOC per Mg of total capacity. No emissions were reported for the vent associated with the caustic scrubber. Another producer reported[3] total process emissions from distillation vents that were calculated to be about 5.3×10^{-3} kg of VOC per Mg of reported capacity (the amount listed in Table IV-1). Information from other producers indicated no existing process emissions.

2. Storage and Handling Emissions

Storage and handling emission sources for a typical hydrocarbon chlorinolysis plant are shown on the flow diagram in Fig. III-1 (sources B and C respectively). Storage tank conditions for the model plant are given in Table IV-2. The uncontrolled storage emissions included in Table IV-1 were calculated, with the emission equations in AP-42,[4] for fixed-roof tanks, half full, and a diurnal temperature variation of 12°C. However, breathing losses were divided by 4 to account for recent evidence indicating that the AP-42 breathing loss equation overestimates emissions.[5] Emissions from storage included in Table IV-1 are 4.77 kg/hr.

Emissions from storage of feed materials were not included in the model plant because the feed streams (propane and propylene) were assumed to originate from pipelines or pressurized storage, which would not emit VOC. However, the chlorinolysis process can be used as a means of converting waste hydrocarbons from other processes into marketable products. For example, the by-product carbon tetrachloride from methanol hydrochlorination and methyl chlorination can be used as a feed material to the chlorinolysis process. Emissions from the storage of the by-product carbon tetrachloride were reported as part of the methanol hydrochlorination and methyl chloride chlorination processes.[1] One producer operating a chlorinolysis facility reported emissions from feed storage tanks containing a mixture of hydrocarbons. This source of emissions was considered to be waste

Table IV-2. Model-Plant Storage Tank Data[a]

Content	No. of Tanks	Tank Size (m^3)	Turnovers per Year	Bulk Liquid Temperature (°C)
Crude product[b]	1	378	6[c]	38
Carbon tetrachloride	2	76	125	35
Carbon tetrachloride	1	757	25	20
Perchloroethylene	2	76	205	35
Perchloroethylene	1	1892	16	20

[a] Does not include feed tanks, which would be required for storage of liquid waste hydrocarbons from other processes.

[b] Includes all carbon tetrachloride, perchloroethylene, and hex waste generated by the process.

[c] Assumed to operate at nearly constant level.

hydrocarbons from other processes. A detailed description of this source is included in the secondary emissions section (IV-B.4) of this report.

Emissions from loading carbon tetrachloride and perchloroethylene product into tank cars and trucks also were calculated, based on submerged loading into clean tank cars and trucks, and with the equations from AP-42.[4] Loading emissions included in Table IV-1 are 1.2 kg/hr.

3. Fugitive Emissions

Process pumps, valves, and compressors are potential sources of fugitive emissions. The 80,000-Mg/yr plant is estimated to have 30 pumps (including spares), 800 process valves, 12 relief valves, and 1 compressor. The fugitive emissions (J on Fig. III-1) listed in Table IV-1 were determined based on the factors shown in Appendix B.

4. Secondary Emissions

Secondary emissions of VOC can result from the handling and disposal of process waste liquids. Two sources of secondary emissions are the bottoms from the perchloroethylene distillation (Source K, Fig. III-1), which are commonly called hex wastes, and the waste caustic from the caustic scrubber (Source L, Fig. III-1).

One producer reported[6] composition of the hex wastes, or bottoms, from the perchloroethylene distillation to be the following:

Component	Quantity (mole %)
Ethylene dichloride	1.4
β-Trichloroethane	7.2
Perchloroethylene	5.7
1,1,1,2-Tetrachloroethane	7.9
1,1,2,2-Tetrachloroethane	29.1
Pentachloroethane	2.7
Hexachlorobutadiene	27.5
Hexachlorobenzene	14.9
Hexachloroethane	3.6

The amount of hex waste generated in the process was calculated from the reported data[6] to be about 52.0 kg per Mg of plant capacity.

Another producer reported[7] the typical hex waste composition to be:

Component	Quantity (%)
Perchloroethylene	4
Hexachloroethane	16
Hexachlorobutadiene	25
Hexachlorobenzene	53
Others	2

It was reported that loading the hex waste from the perchloroethylene distillation column into trucks for removal to incineration resulted in emissions of less than 1 X 10^{-4} kg of VOC per Mg of capacity. However, uncontrolled emissions from a hex-waste loading operation combined with vented emissions from waste hydrocarbon storage tanks were reported to be 5.6 X 10^{-2} kg per Mg of plant capacity. The composition of this combined source of emissions was reported as follows:[6]

Component	Quantity (mole %)
Vinyl chloride	0.166
Vinylidene chloride	1.306
trans-Dichloroethylene	0.246
cis-Dichloroethylene	0.124
Chloroform	0.037
Ethylene dichloride	2.607
Trichloroethylene	0.058
Carbon tetrachloride	0.112
Propylene dichloride	0.336
β-Trichloroethane	0.239
1,1,1,2-Tetrachloroethane	0.095
1,1,2,2-Tetrachloroethane	0.046
Pentachloroethane	0.009
Nitrogen	94.620

The emission ratio of 5.6 X 10^{-2} kg per Mg of plant capacity is included in Table IV-1 for the combined sources of hex-waste handling and waste hydrocarbon storage emissions, although their amounts and compositions will vary as broadly as the diverse feed materials entering the chlorinolysis reaction. Many producers do not have to store liquid wastes for feed to the process, which would eliminate the storage portion of these emissions.

The common practice of disposal of the hex-wastes by thermal oxidation creates secondary emissions because of incomplete oxidation. Secondary emissions from this source were calculated to be less than 1 X 10^{-3} kg of VOC per Mg of plant capacity based on reported information.[6] Emissions from this source were considered to be included in the hex-waste handling and waste hydrocarbon storage emissions described above.

Secondary emissions from waste caustic were calculated from data reported[3] by one producer to be about 1.1 X 10^{-3} kg of VOC per Mg of plant capacity. Data from another producer[7] indicated the total VOC in aqueous waste discharges to be about 2.9 X 10^{-1} kg per Mg of plant capacity. It was estimated by this second producer that all VOC in the aqueous waste discharge would eventually be emitted to the air.[7] With these two sets of data for secondary wastes assumed to be typical for the industry, an average of the two emissions ratios is about 1.5 X 10^{-1} kg of total VOC per Mg of plant capacity.

Based on the data in Appendix D and on the assumption that the combined production of carbon tetrachloride and perchloroethylene by the chlorinolysis process as calculated from the industry data given in Sect. II was 340,000 Mg/yr in 1979 and that the average industry emissions correspond to the 80,000-Mg/yr plant discussed in this report, the 1979 industry emissions are projected to be about 727 Mg/yr.

C. REFERENCES*

1. F. D. Hobbs and C. W. Stuewe, IT Enviroscience, Inc., Chloromethanes. Methanol Hydrochlorination and Methyl Chloride Chlorination Process (in preparation for EPA, ESED, Research Triangle Park, NC).

2. F. D. Hobbs, IT Enviroscience, Inc., Trip Report on Visit Regarding Geismar, LA Plant of Vulcan Materials Co., Jan. 4, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

3. D. W. Smith, Du Pont, Wilmington, DL, letter to D. R. Goodwin, EPA, Mar. 23, 1978.

4. C. C. Masser, "Storage of Petroleum Liquids," pp 4.3-1—4.3.12 in Compilation of Air Pollutant Emission Factors, AP-42, Part A, 3d ed., EPA (August 1977).

5. E. C. Pulaski, TRW, Inc., letter dated May 30, 1979, to Richard Burr, EPA.

6. P. Reis, Texas Air Control Board, Emissions Inventory Questionnaire, TACB Account Number 104-137-1, Dow Chemical Co., Freeport, TX, data for 1975.

7. J. Beale, Dow Chemical, Midland, MI, letter dated Mar. 1, 1978 to L. Evans, EPA.

8. Thomas A. Robinson, Vulcan Materials Company, Wichita, KS, letter dated July 9, 1979, to David R. Patrick, EPA.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. APPLICABLE CONTROL SYSTEMS

A. PROCESS EMISSIONS

Process emissions as listed in Table IV-1 of this report constitute less than 1% of the total uncontrolled emissions from the hydrocarbon chlorinolysis process. No controls are identified for process emissions.

B. STORAGE EMISSIONS

Uncontrolled storage of intermediates, in-process materials, and final products as listed in Table IV-1 of this report constitutes about 50% of total emissions from the hydrocarbon chlorinolysis process. Refrigerated condensers are used, in some cases in conjunction with pressurized-nitrogen padding, to reduce emissions from carbon tetrachloride storage tanks by 60 to 80%, depending on the design of the control system.[1,2] One such condenser, which was installed in 1975 at a cost of $10,000, reduced emissions by about 10,400 kg/yr with an energy use of about 300 MJ/day.[1] A pressurized-nitrogen padding system was installed on a storage tank in 1968 for $800.[1] Use of 1.36×10^5 Pa pressurized-nitrogen padding on perchloroethylene storage tanks was reported to reduce losses from storage of that material by 35% for a cost of $800 in 1968.[1] With this technique the emissions were reduced by about 2100 kg/yr.[1]

The controlled storage emissions given in Table V-1 were based on 80% control by use of refrigerated condensers. Storage emissions are discussed in detail in a separate report.[3]

C. HANDLING EMISSIONS

No method was reported by the producers surveyed for control of emissions from handling carbon tetrachloride or perchloroethylene product. Handling emissions are discussed in detail in a separate report.[3]

D. FUGITIVE EMISSIONS

Control for fugitive sources is discussed in a document covering fugitive emissions from the synthetic organic chemicals manufacturing industry (SOCMI).[4] The fugitive emissions given in Table V-1 were calculated with the factors given in Appendix B. These factors are based on the assumption that any major leaks will be detected and corrected.

Table V-1. Controlled Emissions[a] from 80,000-Mg/yr Chlorinolysis Process Plant

Emission Source	Stream Designation (Fig. III-1)	Control Device or Technique	Emission Reduction (%)	Emissions	
				Total VOC Ratio (kg/Mg)[b]	Total VOC Rate (kg/hr)
Process vents	A	None		0.0053	0.049
Storage	B	Refrigerated condenser	80	0.10	0.95
Handling	C	None		0.13	1.2
Fugitive	J	Detection and correction of major leaks		0.46	4.19
Feed storage and hex waste handling and disposal	K	Vapor balance[c] and refrigerated condenser	∿99	<0.001	<0.01
Waste caustic	L	Steam stripper	96	0.006	0.056
Total				0.70	6.46

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[a] All emissions are based on 8760 hr of operation per year.

[b] kg of emissions per Mg of combined carbon tetrachloride and perchloroethylene produced.

[c] All emissions eliminated except those from thermal oxidation of the hex wastes.

E. SECONDARY SOURCES

Emissions from loading of hex wastes from the perchloroethylene distillation column into trucks for transport to a thermal oxidizer were reported to have been eliminated by one producer. A vapor-balance system was installed to partially control emissions from hex-waste handling in 1975 at a reported cost of $200,000. Emissions from the hex-waste vapor-balance system were then combined with emissions from storage of waste products that are used as a feed to the reactor and controlled with a refrigerated condenser, which cost $35,000 in 1974. The material exiting the refrigerated condenser was then recycled to the chlorinolysis reactor. The reduction in emissions from use of the two control devices and the eventual recycle was about 6400 kg/yr. About 450 MJ/day is required to operate the refrigerated condenser. The only emissions remaining uncontrolled are those from the thermal oxidizer, which is used to destroy the hex wastes originating at the perchloroethylene distillation column.[1]

Installation of a steam stripper was reported to reduce VOC content in the waste caustic by about 96%. VOC stripped from the waste caustic is recycled to the process.[5] Controlled secondary emissions from the waste caustic listed in Table II-1 are based on installation of a steam stripper.

F. REFERENCES*

1. J. Beale, Dow Chemical, Midland, MI, letter to L. Evans, EPA, Mar. 1, 1978.

2. F. D. Hobbs, IT Enviroscience, Inc., Trip Report on Visit Regarding Geismar, LA, Plant of Vulcan Materials Co., Jan. 4, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

3. D. G. Erikson, Storage and Handling (in preparation for EPA, ESED, Research Triangle Park, NC).

4. D. G. Erikson and V. Kalcevic, Fugitive Emissions (in preparation for EPA, ESED, Research Triangle Park, NC).

5. D. W. Smith, Du Pont, Wilmington, DL, letter to D. R. Goodwin, EPA, Mar. 23, 1978.

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APPENDIX A

Table A-1. Physical Properties of Carbon Tetrachloride and Tetrachloroethylene (Perchloroethylene)

	Carbon Tetrachloride[a]	Tetrachloroethylene[b]
Synonym	Tetrachloromethane, perchloromethane, methane tetrachloride	Perchloroethylene, ethylene tetrachloride, carbondichloride, tetrachloroethene
Molecular formula	CCl_4	C_2Cl_4
Molecular weight	153.82	165.82
Physical state	Liquid	Liquid
Vapor pressure	115.2 mm Hg at 25°C	18.47 mm Hg at 25°C
Vapor specific gravity	5.32	5.83
Boiling point	76.54°C at 760 mm Hg	121.20°C at 760 mm Hg
Melting point	-22.99°C	-19°C
Density	1.5940 g/ml at 20°C/4°C	1.6227 g/ml at 20°C/4°C
Water solubility	Insoluble	Insoluble

[a] From: J. Dorigan et al., "Carbon Tetrachloride," p. AI-222 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Organic Chemicals (Chemicals A-C), MTR-7248, Rev. 1, Appendix I, Mitre Corp., McLean, VA (September 1976).

[b] From: J. Dorigan et al., "Perchloroethylene," p. AIV-24 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Organic Chemicals (Chemicals O-Z), MTR-7248, Rev. 1, Appendix IV, Mitre Corp., McLean, VA (September 1976).

APPENDIX B

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX C

LIST OF EPA INFORMATION SOURCES

D. W. Smith, Du Pont, Wilmington, DL, letter tc D. R. Goodwin, EPA, Mar. 23, 1978.

J. Beale, Dow Chemical, Midland, MI, letter to L. Evans, EPA, Mar. 1, 1978.

J. Beale, Dow Chemical, Midland, MI, letter to L. Evans, EPA, May 5, 1978.

P. Reis, Texas Air Control Board, Emissions Inventory Questionnaire, TACB Account Number 104-137-1, Dow Chemical Co., Freeport, TX, data for 1975.

F. D. Hobbs, IT Enviroscience, Inc., Trip Report on Visit Regarding Geismar, LA, Plant of Vulcan Materials Co., Jan. 4, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

F. D. Hobbs, IT Enviroscience, Inc., Trip Report on Visit Regarding South Charleston, WV, Plant of FMC Corporation, Mar. 14, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

APPENDIX D

EXISTING PLANT CONSIDERATIONS

A. INFORMATION SOURCES

The information used in preparing this report was gathered through a site visit to one manufacturing location[1] and from data supplied by producers.[2—8] Information concerning reported emissions and control techniques known to be in use by industry is presented in this appendix.

1. Dow—Freeport, TX

Refrigerated condensers and pressurized-nitrogen padding are used to reduce emissions from carbon tetrachloride storage, and pressurized-nitrogen padding is used to reduce emissions from perchloroethylene storage. Vapor-balance, refrigerated condensation, and recycle are all used to control emissions from hex-waste handling and feed storage tanks.[3—5]

2. Du Pont—Corpus Christi, TX

This plant reportedly does not use the chlorinolysis process,[7] but it does produce carbon tetrachloride and perchloroethylene co-products[6] and uses caustic scrubbing for treatment of emissions.[2] The VOC is stripped from the waste caustic and recycled to the process.[2]

3. Vulcan—Geismar, LA and Wichita, TX

Process emissions are reduced at both locations by separating inert gases in the hydrogen chloride absorption and chlorine removal systems. At Geismer, LA, excess chlorine is reacted with ethylene dichloride, which is recycled to the chlorinator. The hydrogen chloride and inert gases are sent to the ethylene dichloride oxychlorination process. In Wichita, KS, the hydrogen chloride is removed in an absorption system. The chlorine and inert gases are dried and recycled to the reactor. The reactor purge is diverted to the chlorine sniff plant.[8]

Reflux drums on the carbon tetrachloride and perchloroethylene distillation columns are generally padded with low-pressure nitrogen. Crude product and the more volatile feedstocks are stored in pressurized tanks to control emissions. A refrigerated condenser reduces emissions from carbon tetrachloride storage at Geismar.[8]

4. Estimated Controlled VOC Emissions

It is estimated that about 15% of the total VOC emissions are controlled for the domestic carbon tetrachloride—perchloroethylene chlorinolysis process industry. This is a weighted average of the following individual estimated projections:

Source	VOC Controlled (%)
Process	0
Storage	20
Handling	0
Fugitive	0
Hex-waste handling and disposal and waste hydrocarbon storage	95
Waste caustic	45

B. REFERENCES*

1. F. D. Hobbs, IT Enviroscience, Inc., Trip Report on Visit Regarding Geismar, LA, Plant of Vulcan Materials Co., Jan. 4, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

2. D. W. Smith, Du Pont, Wilmington, DL, Letter dated Mar. 23, 1978, to D. R. Goodwin.

3. J. Beale, Dow Chemical, Midland, MI, letter dated Mar. 1, 1978 to L. Evans, EPA.

4. J. Beale, Dow Chemical, Midland, MI, letter dated May 5, 1978 to L. Evans, EPA.

5. P. Reis, Texas Air Control Board, Emissions Inventory Questionnaire, TACB Account Number 104-137-1, Dow Chemical Co., Freeport, TX, data for 1975.

6. J. R. Cooper, Du Pont, Wilmington, DL, letter dated July 25, 1979, to D. R. Patrick, EPA.

7. J. R. Cooper, Du Pont, Wilmington, DL, letter dated Sept. 27, 1979 to J. R. Farmer, EPA.

8. T. A. Robinson, Vulcan Materials Company, Wichita, KS, letter dated July 9, 1979, to D. R. Patrick, EPA.

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REPORT 3

FLUOROCARBONS
(ABBREVIATED REPORT)

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This report contains certain information which has been extracted from the Chemical Economics Handbook, Stanford Research Institute. Wherever used, it has been so noted. The proprietary data rights which reside with Stanford Research Institute must be recognized with any use of this material.

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1×10^{12} grams
G	giga	10^{9}	1 Gg = 1×10^{9} grams
M	mega	10^{6}	1 Mg = 1×10^{6} grams
k	kilo	10^{3}	1 km = 1×10^{3} meters
m	milli	10^{-3}	1 mV = 1×10^{-3} volt
μ	micro	10^{-6}	1 μg = 1×10^{-6} gram

II. INDUSTRY DESCRIPTION

A. INTRODUCTION

Fluorocarbon production was selected for study because preliminary estimates indicated that emissions of volatile organic compounds (VOC) are high and because the chlorinated hydrocarbon raw materials are relatively toxic. Fluorocarbons may also play a role in the destruction of the earth's ozone layer.

There are five major fluorocarbons that represent at least 95% of the total production of fluorinated hydrocarbons: trichlorofluoromethane (fluorocarbon 11), dichlorodifluoromethane (fluorocarbon 12), trichlorotrifluoroethane (fluorocarbon 113), dichlorotetrafluoroethane (fluorocarbon 114), and chlorodifluoromethane (fluorocarbon 22).[1] The processes for producing these fluorocarbons are described in this report. Other commercially produced fluorocarbons are chloropentafluoroethane (fluorocarbon 115), bromotrifuloromethane (fluorocarbon 13B1), tetrafluoromethane (fluorocarbon 14), and hexafluoroethane (fluorocarbon 116), which, combined, represent <5% of the total fluorocarbon production and therefore are not considered in this report.[1]

Fluorocarbons 12, 22, and 114 are gases at ambient temperature, and fluorocarbons 11 and 113 are liquids. Appendix A lists the pertinent physical properties of these five important fluorocarbons.[2]

Fluorocarbons 11 and 12 are normally produced in an integrated facility, as are fluorocarbons 113 and 114. Fluorocarbon 22 is normally produced in its own facility. The production of fluorocarbons involves the use of anhydrous hydrogen fluoride (HF) to successively replace chlorine with fluorine.

B. USAGE AND GROWTH

Approximately $400 million worth of fluorocarbons was consumed in 1977. This total includes the estimated value of captive consumption by basic producers.[3] At an average price of $0.88 per kg this amounts to a total consumption of 454 Gg in 1977.

Historically, about 50% of all fluorocarbons produced have been used as aerosol propellants. However, the ozone controversy, which began in late 1974, has caused a decline in the use of aerosols and therefore a decrease in fluorocarbon consumption for this application to approximately 24% in 1978. The principal compounds used as aerosol propellants are fluorocarbons 11, 12, 113, and 114.[2—4]

Nonessential uses of fluorocarbon propellants were scheduled to be banned in 1978. The first phase of the EPA's program was that manufacturers stop making fluorocarbons for aerosols by October 1978. Approximately 2 or 3% of the original fluorocarbons used as propellants were considered to be essential. The use of fluorocarbons as propellants was estimated to shrink to this level by 1979.[4]

Refrigerants, now the largest application for fluorocarbons, account for an estimated 39% of the consumption, up from a historical level of 30%. Fluorocarbon refrigerants are expected to have a slow but steady growth through 1981. The refrigerant most commonly employed is fluorocarbon 12, found in most home refrigerators and many commercial freezer and display cases. Much of the air conditioning industry is served by fluorocarbon 22 for small equipment and fluorocarbon 11 for large centrifugal compressors.[2—4]

Other significant uses of fluorocarbons are as blowing agents, plastics, and solvents. Specifically, fluorocarbon 11 is used as a blowing agent to increase the thermal insulation properties of urethane foams. The overall consumption of fluorocarbons is forecast to remain relatively level until 1980, with the decline of aerosol propellants being offset by the increasing use of fluorocarbons as refrigerants, blowing agents, and plastic materials.[2,3] A slow but steady growth rate of 5 or 6% from 1980 to 1983 is forecast for all fluorocarbons.[4]

C. DOMESTIC PRODUCERS

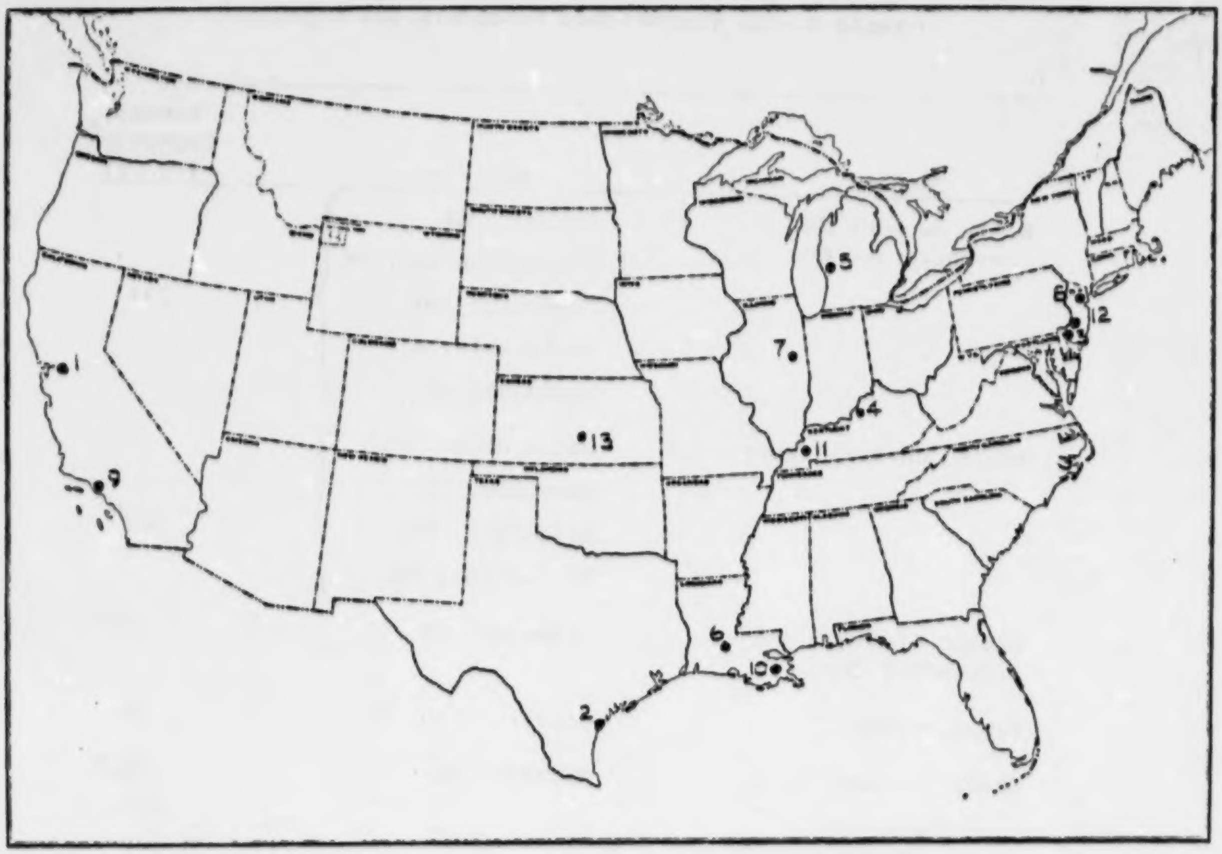
There are 5 major producers of fluorocarbons in the United States at 12 plants. Supply and demand came into better balance in 1978 with the prior closing of plants by Du Pont, Penwalt, and Union Carbide. Table II-1 lists the producers, plant locations, and overall annual 1979 capacities for each company. The locations[4] of fluorocarbon production facilities are shown in Fig. II-1.

Table II-1. Flurocarbon Producers and Capacities

Company	Location	Annual Capacity[a] (Gg/yr)
E. I. du Pont de Nemours and Co.	Antioch, CA	227
	Corpus Christi, TX	
	Deepwater, NJ	
	Louisville, KY	
	Montague, MI	
Allied Chemical Corp.	Baton Rouge, LA	182[b]
	Danville, IL	
	Elizabeth, NJ	
	El Segundo, CA	
Kaiser Aluminum and Chemical Corp.	Gramercy, LA	29.5
Penwalt Corp.	Calvert City, KY	36
Essex Chemical Corp.	Wichita, KA	20.5
Total		495

[a] 1979 capacity does not include plants closed by Du Pont, Penwalt, and Union Carbide.

[b] Includes some capacity that has been added at Baton Rouge, LA, and Elizabeth, NJ.



1. Dupont, Antioch, CA
2. Dupont, Corpus Christi, TX
3. Dupont, Deepwater, NJ
4. Dupont, Louisville, KY
5. Dupont, Montague, MI
6. Allied, Baton Rouge, LA
7. Allied, Danville, IL
8. Allied, Elizabeth, NJ
9. Allied, El Segundo, CA
10. Kaiser, Gramercy, LA
11. Penwalt, Calvert City, KY
12. Penwalt, Thorofare, NJ
13. Essex, Wichita, KS

Fig. II-1. Locations of Fluorocarbons Manufacturing Facilities

Data for 1978 indicated an estimated total production of 413 Gg split as follows: 159 Gg for fluorocarbon 12; 89 Gg for fluorocarbon 11; 91 Gg for fluorocarbon 22; and 74 Gg for other fluorocarbons, which include fluorocarbons 113, 114, and 115. Therefore fluorocarbons 12, 11, and 22 have been estimated to represent 82% of the total 1978 fluorocarbon production.[5]

D. REFERENCES*

1. R. F. Bradley, "Fluorinated Hydrocarbons——Salient Statistics," p. 658.2030C in *Chemical Economics Handbook*, Stanford Research Institute, Menlo Park, CA (September 1975).

2. R. C. Downing, "Fluorinated Hydrocarbons," pp. 739—747 in *Kirk-Othmer Encyclopedia of Chemical Technology*, 2d ed., vol. 9, edited by A. Standen *et al*., Wiley-Interscience, New York, 1966.

3. "Fluorocarbons," pp. 141, 142 in *Kline Guide to the Chemical Industry*, 3d ed., edited by M. K. Meegan, Charles H. Kline and Co., Fairfield, NJ, 1977.

4. *1979 Directory of Chemical Producers. United States of America*, p. 636, SRI International, Menlo Park, CA.

5. "Fluorocarbons," *Chemical Products Synopsis*, Mannsville Chemical Products, Mannsville, New York, June 1978.

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*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an *additional* reference is required for only a certain *portion* of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

III. PROCESS DESCRIPTIONS

A. INTRODUCTION

As previously discussed, the five major fluorocarbons are F-11, -12, -22, -113, and -114, representing >95% of the total domestic production of fluorinated hydrocarbons.[1] The only commercially important domestic process for the production of fluorocarbons involves the liquid-phase catalytic reaction of anhydrous hydrogen fluoride and chlorinated hydrocarbons. The catalytic vapor-phase reaction has been used commercially, although much less generally than the liquid-phase process. The only foreign process for fluorocarbon production (not being practiced in the United States) involves the single-step reaction of hydrocarbons with chlorine and hydrogen fluoride and eliminates the requirement for an intermediate chlorinated hydrocarbon feedstock. A process based on this type of reaction has been developed by Montedison in Italy. At present there are no known plans to introduce this process domestically.[2] This report covers only the process involving the liquid-phase reaction of hydrogen fluoride and chlorinated hydrocarbons.

B. LIQUID-PHASE REACTION OF HF AND CHLORINATED HYDROCARBONS

1. Basic Process

Fluorocarbons are produced by the following idealized chemical reactions:[1,2]

Fluorocarbons 11 and 12

$$\underset{\text{(carbon tetrachloride)}}{2CCl_4} + \underset{\text{(anhydrous hydrogen fluoride)}}{3HF} \xrightarrow{\text{catalyst}} \underset{\text{(trichlorofluoromethane)}}{CCl_3F} + \underset{\text{(dichlorodifluoromethane)}}{CCl_2F_2} + \underset{\text{(hydrochloric acid)}}{3HCl}$$

Fluorocarbon 22

$$\underset{\text{(chloroform)}}{CHCl_3} + \underset{\text{(anhydrous hydrogen fluoride)}}{2HF} \xrightarrow{\text{catalyst}} \underset{\text{(chlorodifluoromethane)}}{CHClF_2} + \underset{\text{(hydrochloric acid)}}{2HCl}$$

Fluorocarbons 113 and 114

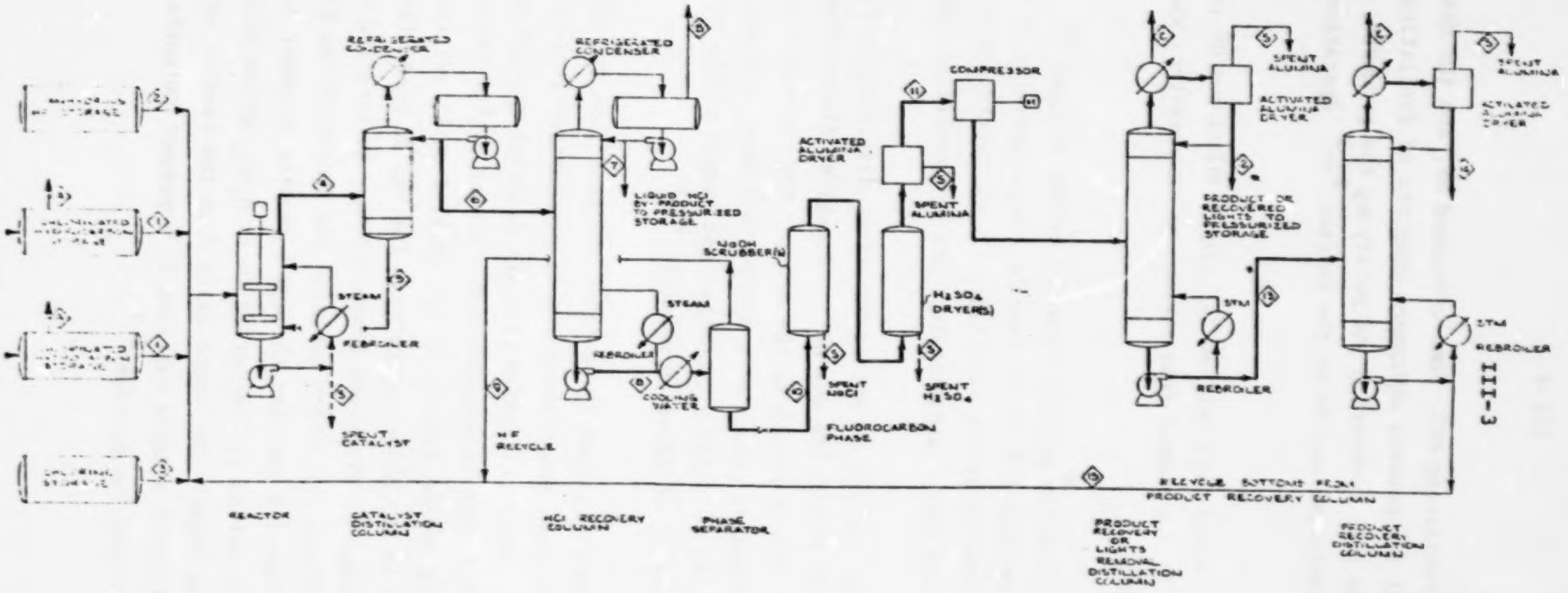
$$\underset{\text{(perchloroethylene)}}{2Cl_2C{=}CCl_2} + \underset{\text{(anhydrous hydrogen fluoride)}}{7HF} + \underset{\text{(chlorine)}}{2Cl_2} \xrightarrow{\text{catalyst}} \underset{\text{(trichlorotrifluoroethane)}}{C_2Cl_3F_3} + \underset{\text{(dichlorotetrafluoroethane)}}{C_2Cl_2F_4} + \underset{\text{(hydrochloric acid)}}{7HCl}$$

Pentavalent antimony functions as the catalyst for all the reactions. Chlorine is added to control the pentavelent activity of the catalyst, which is dissolved in an equilibrium mixture of chlorinated hydrocarbon feed plus partly fluorinated intermediates. Reactor temperatures vary from 45 to 200°C and pressures vary from 1 X 10^5 to 3.5 X 10^6 Pa, depending on the feed and products involved. The specific reaction conditions are discussed extensively in various process patents.[2]

The important 2-carbon-atom fluorocarbons (113 and 114) could be produced from hexachloroethane feed. The high melting point of hexachloroethane (186°C), however, makes it more convenient to use perchloroethylene plus chlorine, as indicated by the third reaction.

The process flow diagram shown in Fig. III-1 represents a typical continuous process for the liquid-phase reaction, whereby any of the three groups of fluorocarbons listed above can be made, depending on the chlorinated hydrocarbon feedstock used. Although the process represented by Fig. III-1 can be block operated to produce each of the three sets of fluorocarbon products, fluorocarbons 11 and 12 are normally produced together in their own facility, as are fluorocarbons 113 and 114. Fluorocarbon 22 is normally produced at its own facility.[2—5]

The liquid-phase process for fluorocarbon manufacture as represented in Fig. III-1 consists basically of a heated reaction vessel containing the catalyst ($SbCl_5$) dissolved in chlorinated feed and partly fluorinated intermediates, to which the feed materials are added in liquid form. The reactor is surmounted by a distillation column and condenser, which separate the reactor vapors into a high-boiling fraction containing catalyst, unreacted chlorinated hydrocarbon, underfluorinated product, and some HF that are returned to the reactor, and into


REFRIGERATED CONDENSER
REFRIGERATED CONDENSER
LIQUID HCl BY-PRODUCT TO PRESSURIZED STORAGE
NaOH SCRUBBER(S)
ACTIVATED ALUMINA DRYER
COMPRESSOR
SPENT ALUMINA
H2SO4 DRYER(S)
SPENT NaCl
SPENT H2SO4
FLUOROCARBON PHASE
STEAM
REBOILER
SPENT CATALYST
STEAM
REBOILER
COOLING WATER
HF RECYCLE
ACTIVATED ALUMINA DRYER
SPENT ALUMINA
PRODUCT OR RECOVERED LIGHTS TO PRESSURIZED STORAGE
STM
REBOILER
SPENT ALUMINA
ACTIVATED ALUMINA DRYER
STM
REBOILER
RECYCLE BOTTOMS FROM PRODUCT RECOVERY COLUMN
REACTOR
CATALYST DISTILLATION COLUMN
HCl RECOVERY COLUMN
PHASE SEPARATOR
PRODUCT RECOVERY OR LIGHTS REMOVAL DISTILLATION COLUMN
PRODUCT RECOVERY DISTILLATION COLUMN

◇ STORAGE EMISSIONS
◇ PROCESS EMISSIONS
* IN THE PRODUCTION OF F-113/114, STREAM 12 IS FED TO THE SECOND PRODUCT RECOVERY COLUMN FOR RECOVERY OF F-114; AND STREAM 13 IS F-113 PRODUCT SENT TO PRESSURIZED STORAGE.

Fig. III-1. Process Flow Diagram for Uncontrolled Fluorocarbons by Liquid-Phase Reaction

Reproduced from best available copy.

an overhead fraction containing HCl, some unreacted HF, and the desired plant products. The rest of the process equipment consists of facilities for separating and recovering the HCl, recovering and purifying the products, and recycling the underfluorinated material and HF to the reactor.[2—5] Operation of the process is as follows:

Dry chlorinated hydrocarbon feed (stream 1), liquid anhydrous HF (stream 2), and chlorine (stream 3) are pumped from storage to the reactor, which contains the catalyst components.

The recycled bottoms from the product recovery column (stream 15) and the HF recycle stream (9) are also fed to the reactor, which operates at a temperature and pressure level dictated by the volatility of the fluorocarbons being produced. The reactor is provided with a steam-heated forced-circulation reboiler.

Vapor from the reactor (stream 4) enters the first distillation-stripping column, which is controlled to remove the net HCl, the desired fluorocarbon products, and some HF overhead and to return to the reactor any vaporized catalyst, unconverted and underfluorinated chlorinated hydrocarbon feed, and some HF (stream 5). The overhead stream (6) is totally condensed and pumped to the HCl recovery column, which operates at an elevated pressure.[2—5]

Anhydrous HCl by-product (stream 7) is taken overhead from the HCl recovery column, totally condensed, and transferred to pressurized storage as a liquid. The inert gases that enter the system with the chlorine gas are purged from the HCl accumulator. This vent is normally not a source of VOC emission. The bottoms from the HCl recovery column (stream 8) are chilled until two liquid phases form, which are separated in the phase separator. The top HF phase (stream 9), which contains a small amount of dissolved fluorocarbons, is recycled to the reactor. The bottom phase (stream 10), which contains the fluorocarbons plus trace amounts of HF and HCl, is expanded and sent through a caustic scrubber to neutralize the HF and HCl. The stream is then dried in an H_2SO_4 drying column followed by an activated alumina dryer. The spent salts from the caustic scrubber and the spent H_2SO_4 and activated alumina (streams 5) represent potential sources of secondary emissions from the process.[2,3]

The neutralized and dried fluorocarbon mixture (stream 11) is compressed and sent to a series of distillation columns to remove the overfluorinated compounds. The products are taken as bottoms or overheads from these distillation columns, depending on the fluorocarbons being produced. In fluorocarbon-12/11 manufacture, fluorocarbon 12 is taken overhead in the first column and the dried product (stream 12) is sent to pressurized storage. The bottoms from this distillation (stream 13) are sent to the second distillation column for removal of fluorocarbon 11 overhead as product (stream 14), which is sent to pressurized storage. As stated previously, the bottoms from the second distillation (stream 15) are recycled to the reactor.[2—5]

In fluorocarbon-22 manufacture, overfluorinated material (fluorocarbon 23) is removed and purged overhead from the first column and fluorocarbon 22 is recovered overhead from the second column.[3,4]

In fluorocarbon-113/114 manufacture, fluorocarbon 113 could be taken off the bottom of the first distillation column after HCl is removed. The overheads from this column could then be fed to the second column for overhead recovery of fluorocarbon 114. Overfluorinated material would be vented from the condenser of the second column. In all cases the gas streams leaving the condensers of the distillation train are potential sources of VOC emissions.[2—5]

C. PROCESS VARIATIONS

A number of process variations exist in the processing of fluorocarbons both between the different fluorocarbon products and among the different producers. In general the number of distillation columns for removal of underfluorinated and overfluorinated material and for product purification and recovery can vary, although two stills are shown in Fig. III-1. Phase separation of HF can take place before or after HCl is removed and will affect the number and type of distillations required.[3,4]

The HCl removal system can vary with respect to the method of removal and the type of by-product acid obtained. Figure III-1 shows the recovery of anhydrous HCl by distillation before phase separation and HF recycle. Other alternatives for HCl recovery and/or removal are the following:[3,4]

1. After anhydrous HCl has been obtained as in Fig. III-1, it can be further purified and absorbed in water to make concentrated technical or food-grade HCl. The absorption step can result in a potential VOC emission.[3—5]
2. The condensed overhead from the catalyst distillation (stream 6 in Fig. III-1) can be treated with water to recover an aqueous solution of HCl contaminated with HF and possibly some fluorocarbons. Phase separation and HF recycle are not carried out if this procedure is employed. The aqueous HCl solution could possibly be sold but is more likely to be disposed of, resulting in a potential secondary emission.[3,4] This procedure is typical of older plants in the industry.
3. In the production of fluorocarbons 113/114, phase separation is commonly carried out before HCl is removed. The HCl is then separated by distillation and combined with the overhead vapor from the fluorocarbon-113 recovery distillation before it is absorbed. As in alternative 2, the aqueous HCl solution obtained can either be sold or be disposed of, depending on the degree of purification and the market for by-product HCl. Disposal could result in secondary emissions.[3,5]

D. REFERENCES*

1. R. F. Bradley, "Fluorinated Hydrocarbons——Salient Statistics," pp. 658.2030A--E in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (September 1975).

2. H. W. Scheeline, Report No. 89. Hydrofluoric Acid and Fluorocarbons, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (November 1973).

3. David M. Pitts, IT Enviroscience, Inc., Trip Report on Site Visit to Allied Chemical Corp., Morristown, NJ, Mar. 16, 1968 (on file at the EPA, ESED, Research Triangle Park, NC).

4. Donald W. Smith, E. I. du Pont de Nemours & Company, letter dated Aug. 21, 1978, regarding fluorocarbon manufacture at the Louisville plant, in response to EPA's request for information on emissions data on fluorocarbon production facilities.

5. Donald W. Smith, E. I. du Pont de Nemours & Company, letter dated June 7, 1978 regarding fluorocarbon process emissions at the Chambers Works, Corpus Christi, Montague, and Antioch plants, in response to EPA's request for information on emissions data on fluorocarbon production facilities.

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IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation. It should be noted that although fluorocarbons 11, 12, 23, 113, 114, and 115 are included in VOC emission totals in this report, they do not, based on current research data, participate in ozone-forming reactions to an appreciable extent.

A. TYPICAL PLANTS

The capacity of the typical integrated plant for the production of fluorocarbons 11 and 12 is 7576 kg/hr total, or 66.36 Gg/yr based on 8760* hr of operation per year. The capacity of the typical plant for the production of fluorocarbon 22 is 947 kg/hr, or 8.3 Gg/yr based on 8760* hr of operation per year. The capacity of the typical integrated plant for the production of fluorocarbons 113 and 114 is 2200 kg/hr total, or 19.3 Gg/yr based on 8760 hr of operation per year. These plants all use the typical process described in Sect. III.

B. PROCESS SOURCES AND EMISSIONS

As indicated in Fig. III-1, three potential sources of process emissions in the manufacture of the fluorocarbons are considered in this report. The vent (B, Fig. III-1) from the HCl recovery column accumulator purges noncondensables and the very small amounts of inert gases entering the system with the chlorine gas.[1—3] No data are available on the emissions from that source, which has the potential to emit minimum boiling azeotropes of the highly fluorinated ethanes and methanes if they are formed in the reactor. The two vents (C, Fig III-1) from the product recovery distillation columns purge the overfluorinated lights and possibly some product from the system and do represent sources of VOC emissions. The emissions from these vents vary among the different products and may be handled differently by different producers.[1—3] The composition of the emissions varies among producers, and even more so between older and newer plants. Optimization of catalyst activity to obtain the maximum yield of product at a high reaction rate is very important in plant operation and hence is considered to be confidential information. Differences in how catalyst activity is controlled will be reflected in the differences in the emissions. Emission rates for the liquid-phase fluorocarbon process as a function of fluorocarbon products produced and typical production rates for each fluorocarbon process are summarized in Table IV-1.

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*Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations the error introduced by assuming continuous operation is negligible.

1. Fluorocarbons-12/11 Process Emissions

In the production of fluorocarbons 11 and 12, gases are purged from the overhead stream from the first distillation, the fluorocarbon-12 recovery column. This emission contains fluorocarbon 12, inert gases such as air, and any fluorocarbon 13 that has been produced. Uncontrolled emissions from this source have been calculated from measured composition data on controlled emissions[1,3] and are based on the operating conditions given in the report[4] on production of hydrofluoric acid and fluorocarbons. The composition of and the emission rate for the uncontrolled emissions are summarized in Table IV-2.

2. Fluorocarbon-22 Process Emissions

In the production of fluorocarbon 22 any overfluorinated material (fluorocarbon 23) produced is vented from the first distillation column, the fluorocarbon-23 separation column, along with inert gases and some fluorocarbon 22. Fluorocarbon 22 and inert gases are vented from the condenser of the second distillation, the fluorocarbon-22 purification column. Uncontrolled emissions from these sources have been calculated from data on the measured amounts of fluorocarbon-23 generation[1] and from composition data based on estimated amounts of inert gases and vapor pressure.[2] The typical uncontrolled composition and combined emission rate for these sources are summarized in Table IV-3.

Table IV-1. Summary of Uncontrolled VOC Emissions from Fluorocarbon Processes

		Emissions					
		From F-12/11; PR,[a] 7576 kg/hr		From F-22; PR, 947 kg/hr		From F-113/114; PR, 2200 kg/hr	
Source	Vent Designation (Fig.III-1)	Ratio[b] (kg/kg)	Rate (kg/hr)	Ratio[b] (kg/kg)	Rate (kg/hr)	Ratio[b] (kg/kg)	Rate (kg/hr)
Distillation vents	C	0.00293	22.48	0.01647	15.6	0.00542	11.93
Storage (raw material)	A	0.000185	1.40	0.00254	2.41	0.00118	2.59
Total		0.00312	23.88	0.01901	18.01	0.0066	14.52

[a] PR = production rate.

[b] kg of VOC per kg of fluorocarbons(s) produced.

Table IV-2. Fluorocarbon-12/11 Uncontrolled Process Emissions from Fluorocarbon-12 Distillation[a]

Component		Composition (wt %)	Emission Rate[b] (kg/hr)
Fluorocarbon 12	VOC	95.05	22.26
Fluorocarbon 13		0.94	0.22
Total VOC		95.99	22.48
Inert gases		4.01	0.94
Total		100.0	23.42

[a] From refs 1 and 3.

[b] Based on typical production capacity of 7576 kg/hr of total fluorocarbons 11 and 12.

Table IV-3. Fluorocarbon-22 Uncontrolled Process Emissions from Fluorocarbon-23/22 Distillations[a]

Component		Composition (wt %)	Emission Rate[b] (kg/hr)
Fluorocarbon 23	VOC	62.6	10.4
Fluorocarbon 22		31.3	5.2
Total VOC		93.9	15.6
Inert gases		6.1	1.0
Total		100.0	16.6

[a] From refs 1 and 2.

[b] Based on typical production capacity of 947 kg/hr of fluorocarbon 22.

3. Fluorocarbon-113/114 Process Emissions

In the production of fluorocarbons 113/114, inert gases and overfluorinated fluorocarbons are purged from the product recovery distillation columns (vents C, Fig. III-1). The actual configuration of the distillation train for recovery of products in a facility designed specifically to produce fluorocarbons 113 and 114 would be somewhat different from the two-column operation presented in Fig. III-1, which is meant to represent a typical general fluorocarbons plant. In practice, all overfluorinated fluorocarbons produced will be emitted to the atmosphere from the distillation train no matter what the configuration. Variance will be with respect to the amount of product fluorocarbon 114 emitted.[1,3]

Reported emissions based on measured composition data from the product recovery distillation vents are summarized in Table IV-4 based on a facility with a typical combined production rate of 2200 kg/hr for fluorocarbons 113 and 114.[1] These data reflect the use of a proprietary process system that is reported to reduce the amount of fluorocarbon 114 emitted.

C. STORAGE EMISSIONS

Emissions result from storage of the chlorinated hydrocarbon raw materials. Storage emission sources for the typical fluorocarbons plant are shown in Fig. III-1 (streams A). Emission estimates, based on calculations of the uncontrolled breathing and working losses associated with raw material storage in fixed-roof tanks, are presented in Table IV-5 for each of the fluorocarbons processes discussed in this report.[1—3] The plant capacities associated with the data are also given in Table IV-5. The bases and assumptions for the information in Table IV-5 (tank sizes, turnovers, temperature variations, etc.) were not given by the manufacturers who made the estimates. Because they are stored in pressure vessels, no emissions are associated with the storage of fluorocarbon products.

Table IV-4. Fluorocarbon-113/114 Uncontrolled Process Emissions from Product Recovery Distillations[a]

Component		Composition (wt %)	Emission Rate[b] (kg/hr)
Fluorocarbon 114	VOC	21.7	6.3
Fluorocarbon 13		14.8	4.3
Fluorocarbon 115		0.9	0.26
Fluorocarbon 124		2.3	0.66
Fluorocarbon 123		0.1	0.04
Higher boilers		1.3	0.37
Total VOC		41.1	11.93
Inert gases		58.9	17.05
Total		100	28.98

[a] From ref 1.

[b] Based on typical production capacity of 2200 kg/hr total for fluorocarbons 113 and 114.

Table IV-5. Uncontrolled Raw-Material Storage Emissions[a]

Product	Raw Material	Emissions Ratio[b] (kg/kg)	Emissions Rate (kg/hr)
Fluorocarbons 12/11	Carbon tetrachloride	0.000185	1.40[c]
Fluorocarbon 22	Chloroform	0.00254	2.41[d]
Fluorocarbons 113/114	Perchloroethylene	0.00118	2.59[e]

[a] From ref 1.

[b] kg of emission per kg of fluorocarbon produced.

[c] Based on total production rate of 7576 kg/hr.

[d] Based on total production rate of 947 kg/hr.

[e] Based on total production rate of 2200 kg/hr.

E. REFERENCES*

1. David M. Pitts, IT Enviroscience, Inc., Trip Report on Site Visit to Allied Chemical Corp., Morristown, NJ, Mar. 16, 1978 (on file at the EPA, ESED, Research Triangle Park, NC).

2. Donald W. Smith, E. I. du Pont de Nemours & Company, letter dated Aug. 21, 1978, regarding fluorocarbon manufacture at the Louisville plant, in response to EPA's request for information on emissions data on fluorocarbon production facilities.

3. Donale W. Smith, E. I. du Pont de Nemours & Company, letter dated June 7, 1978, regarding fluorocarbon process emissions at the Chambers Works, Corpus Christi, Montague, and Antioch plants, in response to EPA's request for information on emissions data on fluorocarbon production facilities.

4. H. W. Scheeline, Hydrofluoric Acid and Fluorocarbons, Report No. 89, Process Economics Program, Stanford Research Institute, Menlo Park, CA (November 1973).

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V. APPLICABLE CONTROL SYSTEMS

A. EMISSION CONTROL FOR TYPICAL PLANTS

1. Process Emissions

As is indicated in Sect. IV, the process emissions from the liquid-phase fluorocarbon processes consist of product and overfluorinated by-products that emerge overhead from the product recovery and/or lights removal distillations. The information available from the industry indicates that condensation, absorption, and product recycle are used to control product emissions. No add-on control technologies are used for the control of by-product (overfluorinated fluorocarbons) emissions, which are dependent on reaction conditions and the amount of overfluorinated material produced. Reaction conditions are normally manipulated to inhibit the formation of overfluorinated materials to the extent possible.[1—3]

In the production of fluorocarbons 11 and 12 Allied Chemical Co. uses a small purge condenser with -20.5°C brine coolant and a carbon tetrachloride feedstock scrubber to remove fluorocarbon 12 and some of the fluorocarbon 13 present from the fluorocarbon-12 distillation vent. The emissions reported from the scrubber vent are 3.04 kg/hr of fluorocarbon 12, 0.03 kg/hr of fluorocarbon 13, and 0.171 kg/hr of carbon tetrachloride based on the typical total production rate of 7576 kg/hr. Some carbon tetrachloride, however, is traded for the fluorocarbon recovered in the emission resulting from this control system, thus reducing the actual total VOC reduction efficiency. For this particular case condensation at -17.8°C at the system pressure has been estimated to have an overall VOC removal efficiency of 83.5%. The removal efficiency of a condenser is a function of the temperature and pressure at which it is operated, and higher efficiencies are possible. The total system, including the condenser and carbon tetrachloride scrubber, is estimated to reduce fluorocarbon emissions by 86.3% and overall VOC emissions by 85.5%. Allied has estimated that this system has an efficiency of 99% based on the removal of fluorocarbon 12 only. No cost information on this control system was obtained.[1]

In the production of fluorocarbon 22 Allied uses a refrigerated purge condenser to recover fluorocarbon 22 from the inert gases and fluorocarbon 23 vented from the fluorocarbon-23 distillation column. This condenser is estimated to be 75% efficient with respect to recovery of fluorocarbon 22. However, since virtually all the fluorocarbon 23 made in the process is vented, the condenser is estimated to be only 25% efficient with respect to overall VOC removal.[1]

Allied controls the emission from the fluorocarbon-22 distillation column by recycling the vent stream from the condenser back to the compressor. Du Pont data indicate that they recover fluorocarbon 23 by condensation after the low boilers are removed and before fluorocarbon 22 is recovered. The refrigerated vent condenser is reported to be 80% efficient with respect to fluorocarbon-23 and overall VOC removal. A refrigerated condenser is also used to recover fluorocarbon 22 from the fluorocarbon-22 recovery and purification system vent. This condenser is reported to be 76% efficient with respect to fluorocarbon-22 and overall VOC removal. No cost data were obtained on these condenser systems.[2]

In the production of fluorocarbons 113/114 Allied uses a proprietary process modification to recover fluorocarbon 114 from the overfluorinated materials vented from the process.[1] In all fluorocarbon production refrigerated vent condensers could be used to reduce the emissions of the overfluorinated by-products, which are normally vented. These recovered materials would then have to be decomposed or disposed of in another manner.

2. Storage Emissions

Emissions of chlorinated hydrocarbon raw materials can be reduced by the use of refrigerated condensers on the storage tank vents. Du Pont reports that a condenser using -17°C brine removes 66% of the chloroform emissions from the chloroform storage tank in the fluorocarbon-22 process.[2]

3. Current Emission Controls

Emission control devices currently used by some domestic commercial fluorocarbon producers are shown in Appendix B.

4. Industry Emissions

From emission data reported by commercial fluorocarbon manufacturers[1—3] emission ratios as a function of fluorocarbon produced have been estimated and are shown in Table V-1. Secondary and fugitive emissions are not considered.

Table V-1. Estimated Emission Ratios for Industry

	Emission Ratios (g/kg)[a] for Production of			
Emission Source	F-12/11	F-22	F-113/114	Total Emission Ratios for All Fluorocarbons[b]
Distillation vents	1.68	14.41	5.42	5.15
Raw material storage	0.185	1.70	1.18	0.70
Total[c]	1.87	16.11	6.60	5.85

[a] g of VOC emission per kg of fluorocarbon produced; determined from refs 1 and 2.

[b] Based on the following 1978 production ratios: F-12/11, 60% F-22, 22%; F-113/114, 18%.

[c] Excluding fugitive and secondary emissions.

The values indicate that, overall, the fluorocarbon processes are ~19% controlled with respect to VOC based on the production ratios given in Table V-1. From the data in Table V-1 and the 1979 total fluorocarbon production of 495 Gg, the emissions from the fluorocarbon industry have been estimated to be 2.90 Gg for 1979. This estimate does not include secondary, fugitive, or handling emissions.

B. REFERENCES*

1. David M. Pitts, IT Enviroscience, Inc., Trip Report on Site Visit to Allied Chemical Corp., Morristown, NJ, Mar. 16, 1978 (on file at the EPA, ESED, Research Triangle Park, NC).

2. Donald W. Smith, E. I. du Pont de Nemours & Company, letter dated Aug. 21, 1978, regarding fluorocarbon manufacture in response to EPA's request for information on emission data on fluorocarbon production facilities.

3. Donald W. Smith, E. I. du Pont de Nemours & Company, letter dated June 7, 1978, regarding fluorocarbon process emissions at the Chambers Works, Corpus Christi, Montague, and Antioch plants, in response to EPA's request for information on emission data on fluorocarbon production facilities.

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APPENDIX A

Table A-1. Physical Properties of Fluorocarbon Compounds[a]

Fluorocarbon Designation	Chemical Name	Molecular Formula	Molecular Weight	Boiling Point (°C)	Melting Point (°C)	Liquid Density (g/ml at °C)	Solubility in Water at 25°C, 1 atm (wt %)	Vapor Pressure[b]
F-11	Trichlorofluoromethane	CCl_3F	137.38	23.8	-111	1.476/25	0.11	1 atm at 23.7°C
F-12	Dichlorodifluoromethane	CCl_2F_2	120.93	-29.8	-158	1.311/25	0.028	5 atm at 16.1°C
F-22	Chlorodifluoromethane	$CHClF_2$	86.48	-40.8	-160	1.194/25	0.30	10 atm at 24°C
F-113	Trichlorofluoroethane	$C_2Cl_3F_3$	187.39	47.6	-35	1.565/25	0.017	400 mm Hg at 30.2°C[c]
F-114	Dichlorotetrafluoroethane	$C_2Cl_2F_4$	170.94	3.8	-94	1.456/25	0.013	2 atm at [illegible]

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[a] R. C. Downing, "Fluorinated Hydrocarbons," pp. 744, 745 in Kirk-Othmer Encyclopedia of Chemical Technology, 2nd ed., Vol. 9, edited by A. Standen *et al.*, Interscience, New York, 1966.

[b] "Vapor Pressure (for) Inorganic Compounds. Pressure Greater Than One Atmosphere," p. D-136 in CRC Handbook of Chemistry and Physics, 48th ed., edited by R. C. Weast and S. M. Selby, The Chemical Rubber Co., Cleveland, 1967.

[c] P. E. Liley, Y. S. Touloukion, and W. R. Gambill, "Physical and Chemical Data," pp. 3--58 in Perry's Chemical Engineers' Handbook, 4th ed., edited by R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick, McGraw-Hill, New York, 1963.

Appendix B

Table B-1. Existing Industrial Emission Control Devices

Producer	Emission Source	Control Device
Allied Chemical Corp.[a]	Distillation vents (2)	(1) Refrigerated vent condenser and scrubber (2) Product recycle
	Storage vents	None
Du Pont[b]	Distillation vents (2)	(1) Refrigerated vent condenser (2) By-product (F-23) recovery
	Storage vents	Refrigerated vent condenser

[a] See ref 1.

[b] See ref 2.

REPORT 4

1,1,1-TRICHLOROETHANE
AND
PERCHLOROETHYLENE, TRICHLOROETHYLENE, AND VINYLIDENE CHLORIDE (ABBREVIATED REPORT)

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ENVIRONMENTAL PROTECTION AGENCY
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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	$(°C \times 9/5) + 32$
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1×10^{12} grams
G	giga	10^{9}	1 Gg = 1×10^{9} grams
M	mega	10^{6}	1 Mg = 1×10^{6} grams
k	kilo	10^{3}	1 km = 1×10^{3} meters
m	milli	10^{-3}	1 mV = 1×10^{-3} volt
μ	micro	10^{-6}	1 μg = 1×10^{-6} gram

II. INDUSTRY DESCRIPTION

A. INTRODUCTION

1,1,1-Trichloroethane (also called methyl chloroform), perchloroethylene, trichloroethylene, and vinylidene chloride are produced as co-products or are produced individually by several processes (see Fig. II-1). The starting raw materials are primarily chlorine and ethylene dichloride, although the flexibility of some of the processes allows other C_2 chlorinated hydrocarbons or waste streams to be used when available. Hydrogen chloride is generated as a by-product from many of the processes and used as a raw material in others. It is also a raw material for the oxychlorination process for producing ethylene dichloride. In order to optimize production economics the hydrogen chloride—generating processes and the hydrogen chloride—consuming processes are usually integrated in a complex where the product or the unwanted by-products and waste streams from one process are utilized as part or all of the raw materials for another process.[1,2]

This report discusses the emissions and control options for the processes for production of 1,1,1-trichloroethane from vinyl chloride and from ethane. Also covered, in abbreviated form, are the chlorination and oxychlorination processes for producing perchloroethylene and trichloroethylene as co-products and the process for production of vinylidene chloride from 1,1,2-trichloroethane. The process for producing 1,1,1-trichloroethane from vinylidene chloride reportedly is on standby.[1] Although the uncontrolled emissions from the processes producing perchloroethylene and trichloroethylene are estimated to be large, they are controlled to a reasonable degree in existing production facilities, and little or no growth is projected for perchloroethylene and trichloroethylene production. A previous product report[3] covered the chlorinolysis of hydrocarbons (and their partially chlorinated derivatives) at or close to pyrolytic conditions to produce perchloroethylene and carbon tetrachloride as co-products. The production of ethylene dichloride is covered in another product report,[4] and the pyrolysis of ethylene dichloride to vinyl chloride is described in several EPA documents.[5,6] Perchloroethylene and trichloroethylene have been produced in the past by chlorination of acetylene but the high cost of acetylene has caused all domestic plants to be shut down, the last one in 1978.[1]

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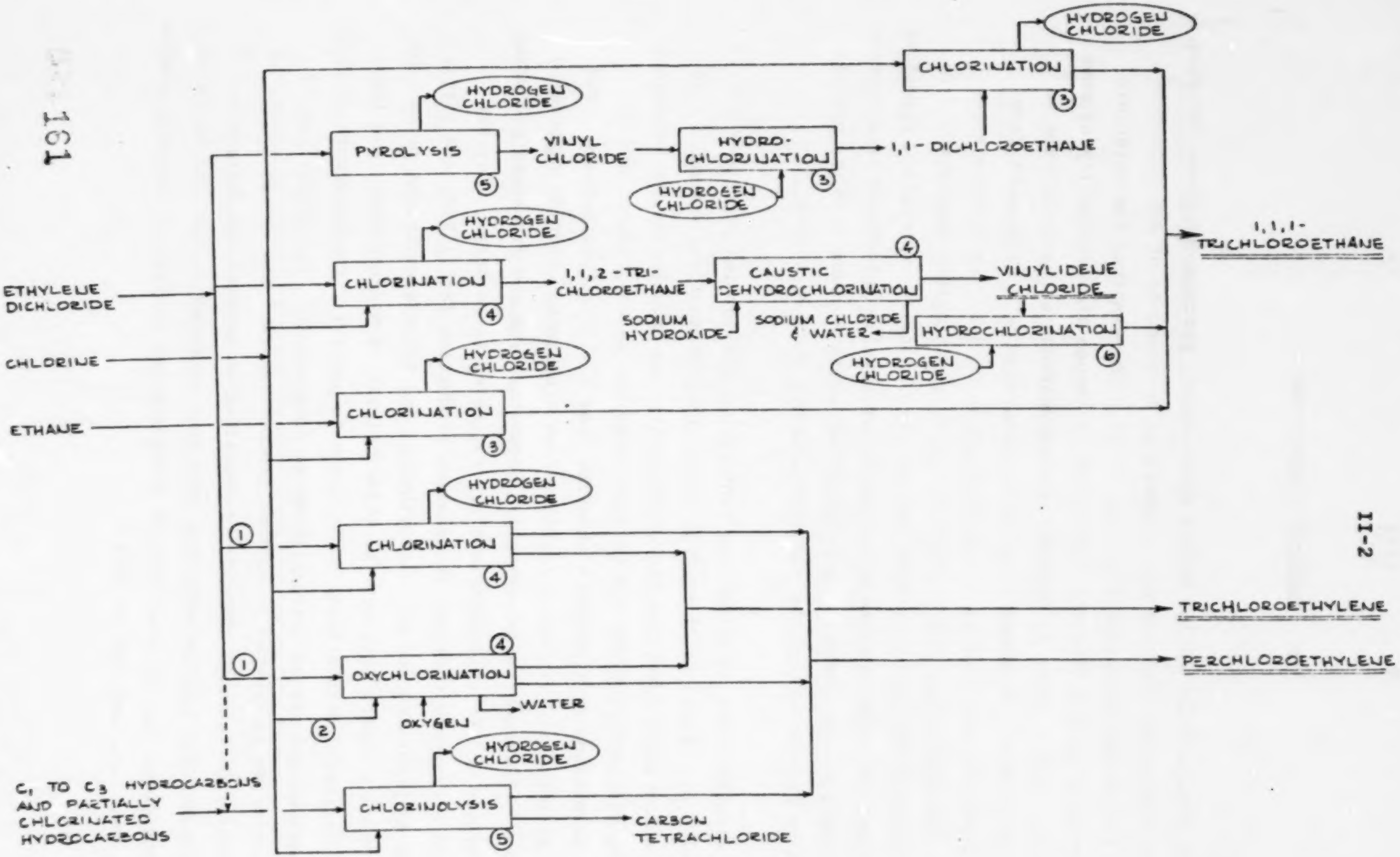
ETHYLENE DICHLORIDE
CHLORINE
ETHANE
C1 TO C3 HYDROCARBONS AND PARTIALLY CHLORINATED HYDROCARBONS
PYROLYSIS
HYDROGEN CHLORIDE
VINYL CHLORIDE
HYDRO-CHLORINATION
1,1-DICHLOROETHANE
CHLORINATION
1,1,1-TRICHLOROETHANE
1,1,2-TRI-CHLOROETHANE
CAUSTIC DEHYDROCHLORINATION
SODIUM HYDROXIDE
SODIUM CHLORIDE & WATER
VINYLIDENE CHLORIDE
HYDROCHLORINATION
OXYCHLORINATION
OXYGEN
WATER
CHLORINOLYSIS
CARBON TETRACHLORIDE
TRICHLOROETHYLENE
PERCHLOROETHYLENE
①
②
③
④
⑤
⑥

NOTES:
① OTHER C_2 CHLORINATED HYDROCARBONS MAY ALSO BE USED AS RAW MATERIAL.
② HYDROGEN CHLORIDE MAY ALSO BE USED AS RAW MATERIAL.
③ FULL REPORT
④ ABBREVIATED REPORT
⑤ PREVIOUS REPORT
⑥ PROCESS IS REPORTEDLY ON STANDBY (SEE REF. 1)

Fig. II-1. Processes for Production of 1,1,1-Trichloroethane, Perchloroethylene, Trichloroethylene, and Vinylidene Chloride

1,1,1-Trichloroethane production was selected for study because preliminary estimates indicated relatively high total emissions of volatile organic compounds (VOC), because it was suspected that it causes harmful health effects,[7] and because substantial industry growth was projected. Perchloroethylene and trichloroethylene are included because they are also chlorinated solvents used in metal cleaning and are often produced in the same complex with 1,1,1-trichloroethane. Vinylidene chloride was included because, as a chlorinated C_2 compound, the production processes, emissions, and associated controls are similar to those for the C_2 chlorinated solvents.

1,1,1-Trichloroethane, perchloroethylene, trichloroethylene, and vinylidene chloride are liquids under ambient conditions but are sufficiently volatile for gaseous emissions to occur during production (see Appendix A for pertinent properties). The emissions from their production consist of ethylene dichloride, 1,1,1-trichloroethane, perchloroethylene, trichloroethylene, vinyl chloride, vinylidene chloride, and other chlorinated hydrocarbons.

B. USAGE AND GROWTH[1,2]

Table II-1 shows the end uses of 1,1,1-trichloroethane, perchloroethylene, trichloroethylene, and vinylidene chloride and their expected growth rates. The predominant use of both 1,1,1-trichloroethane and trichloroethylene is as a metal-cleaning solvent. Although trichloroethylene is the preferred solvent for this application, its use has declined since it was found to contribute to smog formation and to be carcinogenic to mice and possibly also to humans. Perchloroethylene is also used as a metal-cleaning solvent but its major use is as a dry-cleaning and textile-processing solvent. Vinylidene chloride is consumed largely in the production of polyvinylidene copolymers such as Saran® and some modacrylic fibers. Until recently it was also used as a raw material for the production of 1,1,1-trichloroethane. Perchloroethylene and 1,1,1-trichloroethane are used as raw materials for various chemicals. 1,1,1-Trichloroethane is also used in aerosol propellant formulations, as a solvent in adhesive and coatings formulations, as a drain cleaner, and as a fabric spotting fluid and in many other applications. Trichloroethylene is used as an extractive solvent and as a component of certain drugs.

Table II-1. Usage and Growth of 1,1,1-Trichloroethane, Perchloroethylene, Trichloroethylene, and Vinylidene Chloride*

End Use	1,1,1-Trichloroethane		Perchloroethylene		Trichloroethylene		Vinylidene Chloride	
	Consumption for 1977 (%)	Average Growth for 1977-1982 (%/yr)	Consumption for 1977 (%)	Average Growth for 1977-1982 (%/yr)	Consumption for 1977 (%)	Average Growth for 1977-1982 (%/yr)	Consumption for 1977 (%)	Average Growth for 1977-1982 (%/yr)
Metal cleaning	67	6	16	1	83	0		
Dry cleaning and textile processing			59	-1.5				
Chemical intermediate	2	8	13	5			100	6
Miscellaneous	31	7	12	-1.5	17	-5		

*See refs 1 and 2.

The increases in the consumption of 1,1,1-trichloroethane, perchloroethylene, trichloroethylene, and vinylidene chloride are difficult to predict because all of them are under pressure from governmental organizations charged with maintaining environmental quality and with protecting the workers' health. Because of the uncertainties concerning future regulations, future uses could be considerably different from projections. 1,1,1-Trichloroethane has experienced strong growth as a substitute for trichloroethylene, because trichloroethylene was believed to be a contributor to smog formation and 1,1,1-trichloroethane was believed not to be. Recently, some researchers have claimed that 1,1,1-trichloroethane in the stratosphere can damage the ozone layer, although there is controversy over the validity of these conclusions.[1] Perchloroethylene has been under the same restrictions as any other organic solvent as to the amount emitted in operations involving heating in the presence of oxygen or where it comes in contact with a flame.[1] Now perchloroethylene,[1] trichloroethylene,[1] and vinylidene chloride[2] are under suspicion as carcinogens, although the validity of this finding for perchloroethylene has been challenged.

The domestic production capacity of 1,1,1-trichloroethane in 1977 was estimated to be 313,000 Mg, with approximately 92% of this capacity being utilized. However, since by the end of 1979 the capacity is expected to be about 590,000 Mg/yr, considerable excess capacity will exist in 1982, even with an increase in demand of 5% per year, unless older capacity is shut down. In 1977 perchloroethylene production utilized only about 56% of an estimated capacity of 542,000 Mg, and trichloroethylene production was only about 60% of an estimated capacity of 225,000 Mg. With perchloroethylene expected to show no growth in demand and with trichloroethylene demand expected to drop about 3% per year, there will be considerable excess capacity for both in 1982. Some plants have been shut down or placed on standby. Vinylidene chloride demand is expected to grow about 6% per year. Data are not available on industry vinylidene chloride capacity but the capacity is believed to be adequate to meet demand through 1982. The 1978 production of vinylidene chloride was 81,000 Mg.

C. DOMESTIC PRODUCERS

Table II-2 lists the producers, locations, and capacities of plants producing 1,1,1-trichloroethane, perchloroethylene, trichloroethylene, and vinylidene chloride as of January 1, 1979. Figure II-2 shows the plant locations.[2,8,9]

Table II-2. Production Capacity for 1,1,1-Trichloroethane, Perchloroethylene, Trichloroethylene, and Vinylidene Chloride

Company	Location	1979 Capacity (Mg/yr) 1,1,1-Trichloroethane[a]	Perchloroethylene[a]	Trichloroethylene[a]	Vinylidene Chloride
Diamond Shamrock	Deer Park, TX		75,000	b	
Dow	Freeport, TX	204,000	68,000	68,000	c
	Pittsburg, CA		18,000		
	Plaquemine, LA	136,000	54,000		23,000—45,000
Du Pont	Corpus Christi, TX		73,000		
Ethyl	Baton Rouge, LA		23,000	20,000	
PPG	Lake Charles, LA	159,000	91,000	91,000	88,000[d]
Stauffer	Louisville, KY		32,000		
Vulcan	Geismar, LA	90,000	68,000		
	Wichita, KS		23,000		
Total		589,000	525,000	179,000	c

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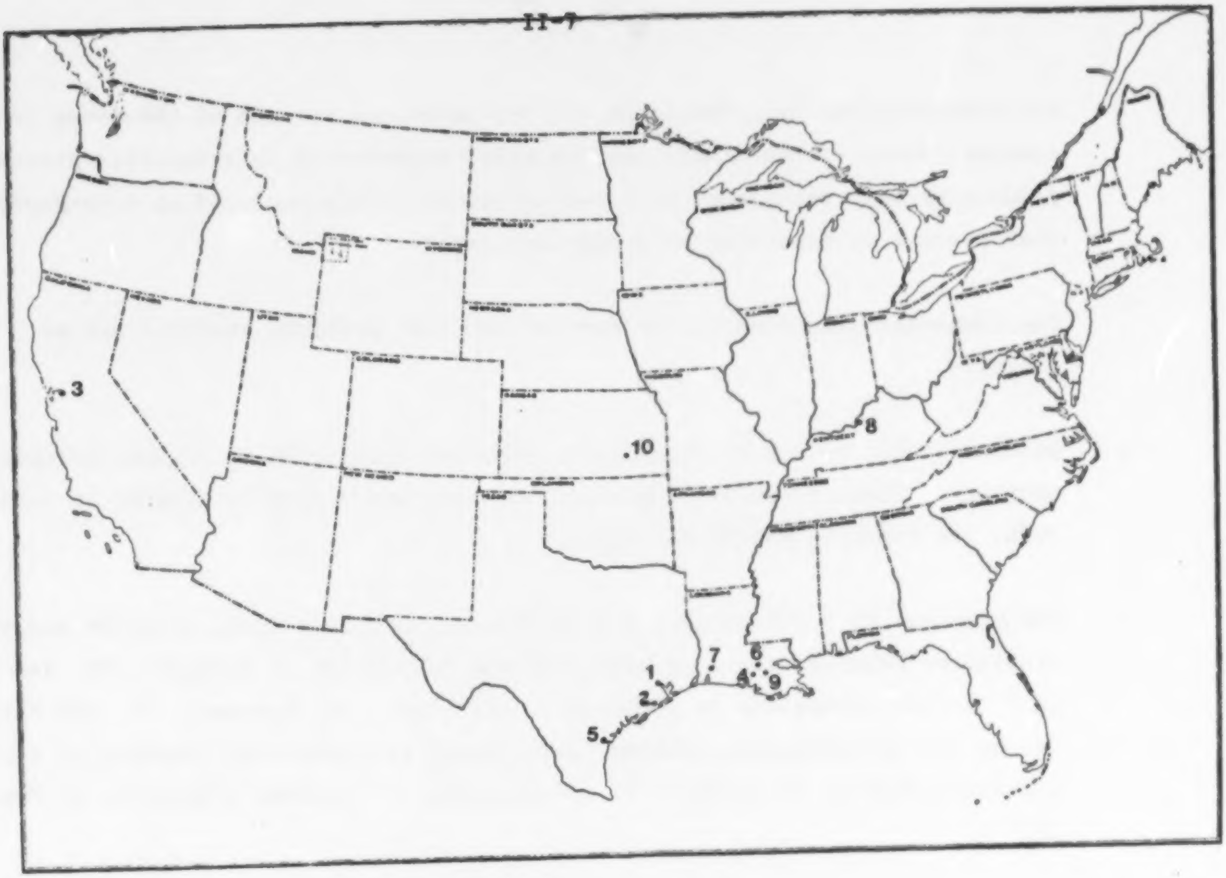
[a] See ref 2.

[b] 23,000-Mg/yr capacity unit placed on standby in early 1978 (ref 2).

[c] Capacity data not available.

[d] Includes 23,000-Mg/yr expansion completed in 1978 (ref 9). Most of this capacity (88,000 Mg/yr) was placed on stand-by with the shutdown of PPG's vinylidene chloride—based 1,1,1-trichloroethane process.



		Chemicals Produced*
(1)	Diamond Shamrock Corp., Deer Park, TX	B
(2)	Dow Chemical Co., Freeport, TX	A-D
(3)	Dow Chemical Co., Pittsburg, CA	B
(4)	Dow Chemical Co., Plaquemine, LA	A,B,D
(5)	Du Pont, Corpus Christi, TX	B
(6)	Ethyl Corp., Baton Rouge, LA	B,C
(7)	PPG Industries, Inc., Lake Charles, LA	A-D
(8)	Stauffer Chemical Co., Louisville, KY	B
(9)	Vulcan Materials Co., Geismar, LA	A,B
(10)	Vulcan Materials Co., Wichita, KS	B

*A = 1,1,1-trichloroethane; B = perchloroethylene; C = trichloroethylene; D = vinylidene chloride.

Fig. II-2. Locations of Plants Manufacturing 1,1,1-Trichloroethane, Perchloroethylene, Trichloroethylene, and Vinylidene Chloride

Perchloroethylene is produced at all ten locations by each of the seven producers; however, seven of the plants use the mixed hydrocarbon chlorinolysis process to produce perchloroethylene, with carbon tetrachloride produced as a co-product. That process is discussed in a previous report.[3]

The companies producing one or more of the four products involved are as follows:

1. Diamond Shamrock Corp.——Chlorinates ethylene dichloride to produce perchloroethylene. Their trichloroethylene production was placed on standby in early 1978; the capacity was 23,000 Mg/yr.[2]

2. Dow Chemical Co.——Produces 1,1,1-trichloroethane from vinyl chloride and produces vinylidene chloride starting with ethylene dichloride at Freeport, TX, and Plaquemine LA.[2] Perchloroethylene is produced at Pittsburg, CA, Freeport, TX, and Plaquemine, LA, by the chlorinolysis process, with carbon tetrachloride produced as a by-product. Trichloroethylene is produced by chlorination of ethylene dichloride at Freeport, TX.[2]

3. Du Pont——Produces perchloroethylene by chlorinolysis of light hydrocarbons, with carbon tetrachloride produced as a co-product. All perchloroethylene output is used in the manufacture of fluorocarbons.[2]

4. Ethyl Corp.——Produces perchloroethylene and trichloroethylene by chlorination of ethylene dichloride.[2]

5. PPG Industries——Produces perchloroethylene and trichloroethylene by oxychlorination of ethylene dichloride; chlorinates ethylene dichloride to 1,1,2-trichloroethane, which is dehydrochlorinated to vinylidene chloride. 1,1,1-Trichloroethane is produced by hydrochlorination of vinyl chloride to 1,1-dichloroethane, followed by chlorination. 1,1,1-Trichloroethane was previously produced from vinylidene chloride. The vinylidene chloride—based process was reportedly placed on standby with the startup of the new vinyl chloride—based process in 1979.[1,2,10]

6. Stauffer Chemical Co.——Produces perchloroethylene and carbon tetrachloride by chlorinolysis of chlorination bottoms.[1]

7. Vulcan Materials Co.——Produces perchloroethylene by chlorinolysis of chlorination bottoms and ethylene dichloride, with carbon tetrachloride produced as a co-product at Geismar, LA, and Wichita, KS. 1,1,1-Trichloroethane is produced by chlorination of ethane at Geismar, LA.[1]

D. REFERENCES*

1. S. A. Cogswell, "C_2 Chlorinated Solvents," pp. 632.3000A—F and 632.3001A—632.3002A in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (December 1978).

2. S. A. Cogswell, "Ethylene Dichloride," pp. 651.5031A—F and 651.5032A—651.5033I in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (February 1979).

3. F. D. Hobbs and C. W. Stuewe, IT Enviroscience, Inc., Carbon Tetrachloride and Perchloroethylene (Hydrocarbon Chlorinolysis Process) (in preparation for EPA, ESED, Research Triangle Park, NC).

4. F. D. Hobbs and J. A. Key, IT Enviroscience, Inc., Ethylene Dichloride (in preparation for EPA, ESED, Research Triangle Park, NC).

5. R. G. Bellamy and W. A. Schwartz, Houdry Div., Air Products and Chemicals, Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry. Volume 8: Vinyl Chloride Manufacture by the Balanced Process, EPA-450/3-7-006-h, Research Triangle Park, NC (July 1975).

6. D. R. Goodwin, Standard Support and Environmental Impact Statement: Emission Standard for Vinyl Chloride, EPA-450/2-75-009, Research Triangle Park, NC (October 1975).

7. "Cancer Warning on Chloroethanes," Chemical Week **123**(10), 21 (Sept. 6, 1978).

8. Arthur D. Little, Inc., Final Report. Vinylidene Chloride Monomer Emissions from the Monomer, Polymer, and Polymer Processing Industries, ADR-76086-31, prepared for EPA Control Systems Laboratory, Durham, NC (April 1976).

9. "Vinylidene Chloride Monomer," p. 80 in 1978 Directory of Chemical Producers, United States of America, Supplement 1, Stanford Research Institute, Menlo Park, CA.

10. F. C. Dehn, PPG Industries, Inc., letter dated Mar. 14, 1979, to EPA in response to request for information on the air emissions from the 1,1,1-trichloroethane, perchloroethylene, and trichloroethylene processes at Lake Charles, LA.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTIONS

A. INTRODUCTION

In this section the processes for producing 1,1,1-trichloroethane from vinyl chloride and from ethane, the chlorination and oxychlorination processes for the production of perchloroethylene and trichloroethylene, and the caustic dehydrochlorination process for production of vinylidene chloride are described. The process for production of 1,1,1-trichloroethane from vinylidene chloride reportedly is on standby[1] and is not described.

B. 1,1,1-TRICHLOROETHANE

1. Introduction

Most of the 1,1,1-trichloroethane produced domestically is made by the vinyl chloride process, with minor amounts made by the ethane process.[1—4] Vinyl chloride, which is produced from ethylene dichloride, is first hydrochlorinated with hydrogen chloride to 1,1-dichloroethane, which is then thermally chlorinated to produce 1,1,1-trichloroethane. The yields from vinyl chloride are over 95%.[5]

With ethane and chlorine as raw materials, 1,1,1-trichloroethane is produced by the noncatalytic chlorination of ethane. Ethyl chloride, vinyl chloride, vinylidene chloride, and 1,1-dichloroethane are also produced, with the relative quantities of the various product fractions being somewhat dependent on operating conditions. When 1,1,1-trichloroethane is the only desired product, vinyl chloride and vinylidene chloride are hydrochlorinated to 1,1-dichloroethane and 1,1,1-trichloroethane respectively, and ethyl chloride and 1,1-dichloroethane are recycled to the chlorination step.[5]

2. Vinyl Chloride Process

Starting with vinyl chloride the following reactions are required to produce 1,1,1-trichloroethane: the hydrochlorination of vinyl chloride to 1,1-dichloroethane and the chlorination of 1,1-dichloroethane to 1,1,1-trichloroethane. The hydrochlorination of vinyl chloride to 1,1-dichloroethane takes place according to the following reaction:

$$\underset{\text{(vinyl chloride)}}{CH_2{=}CHCl} + \underset{\text{(hydrogen chloride)}}{HCl} \xrightarrow{FeCl_3} \underset{\text{(1,1-dichloroethane)}}{CH_3{-}CHCl_2}$$

The chlorination of 1,1-dichloroethane to 1,1,1-trichloroethane takes place according to the following reaction:

$$CH_3\text{-}CHCl_2 \quad + \quad Cl_2 \quad \longrightarrow \quad CH_3\text{-}CCl_3 \quad + \quad HCl$$

(1,1-dichloroethane) (chlorine) (1,1,1-trichloroethane) (hydrogen chloride)

Figure III-1 represents a flow diagram for a process in which 1,1,1-trichloroethane is produced from vinyl chloride.[5,6] Vinyl chloride (stream 1) from storage, hydrogen chloride (stream 2), and the recycled overhead stream (7) from the light-ends column are fed to the hydrochlorination reactor. The reaction is exothermic and takes place at 35 to 40°C in the presence of a catalytic amount of ferric chloride.

Ammonia (stream 4) is added to the reactor effluent (stream 3), forming a solid complex with the residual hydrogen chloride and the ferric chloride catalyst. The complex is removed by the spent catalyst filter as a semisolid waste stream (source G). The filtered hydrocarbon stream (stream 5) passes to the heavy-ends column, where high-boiling chlorinated organics (tars) are removed as a waste stream (source H) from the bottom.

The overhead (stream 6) passes to the light-ends column, where a separation is made between 1,1-dichloroethane and the lighter components, primarily unreacted vinyl chloride. The overhead stream (7) is recycled to the hydrochlorination reactor. The 1,1-dichloroethane product is removed as the bottom stream (8) and transferred to intermediate storage.

1,1-Dichloroethane from intermediate storage and chlorine (stream 9) are combined and fed to the chlorination reactor, where the 1,1-dichloroethane is converted to 1,1,1-trichloroethane. The reaction is exothermic and noncatalytic, occurring at a temperature of about 400°C. The reactor effluent (stream 10) passes to the hydrogen chloride column, where the hydrogen chloride formed in the reaction and some low-boiling organic compounds are removed overhead (stream 11). This stream may be used to supply the hydrogen chloride requirements of other chlorinated organic processes directly (e.g., the ethylene dichloride process) or it may be purified to remove the contained organics before it is used.

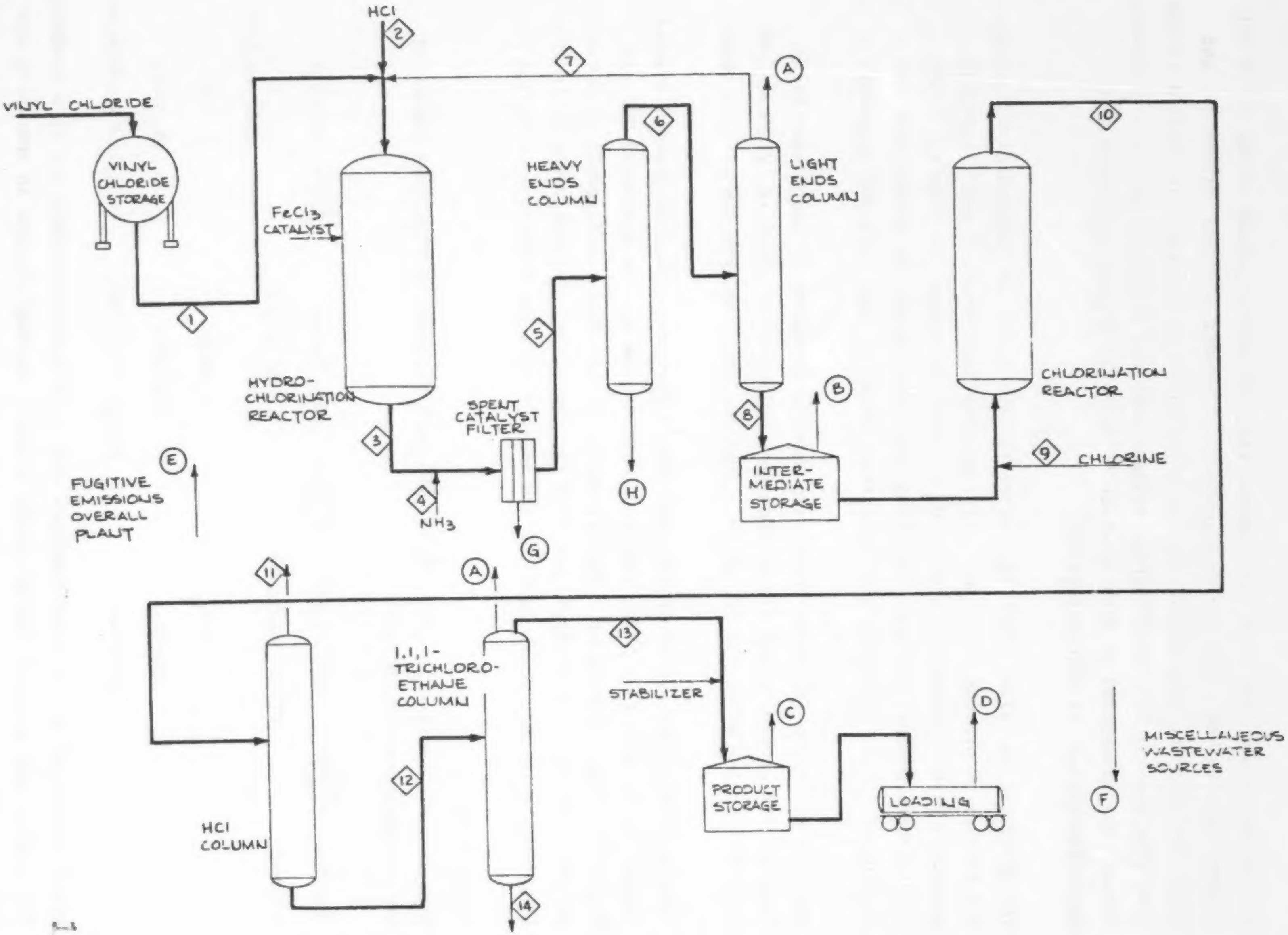
VINYL CHLORIDE
VINYL CHLORIDE STORAGE
1
HCl
2
7
FeCl3 CATALYST
HYDRO-CHLORINATION REACTOR
3
4
NH3
SPENT CATALYST FILTER
G
5
HEAVY ENDS COLUMN
6
H
LIGHT ENDS COLUMN
A
8
INTER-MEDIATE STORAGE
B
CHLORINATION REACTOR
9
CHLORINE
10
FUGITIVE EMISSIONS OVERALL PLANT
E
11
HCl COLUMN
12
1,1,1-TRICHLORO-ETHANE COLUMN
A
13
14
STABILIZER
PRODUCT STORAGE
C
LOADING
D
MISCELLANEOUS WASTEWATER SOURCES
F

Fig. III-1. Flow Diagram for 1,1,1-Trichloroethane from Vinyl Chloride

The bottom stream (12) from the hydrogen chloride column passes to the 1,1,1-trichloroethane column. The purified product is removed overhead (stream 13) and, after the addition of a stabilizer, is transferred to storage. The bottom stream (14) from the 1,1,1-trichloroethane column, composed primarily of 1,1,2-trichloroethane, is transferred as feed to other chlorinated organic processes (e.g., perchloroethylene-trichloroethylene).

The distillation column vents (A), which release primarily noncondensable gases, are sources of process emissions. Storage emissions (vents B and C) include emissions from intermediate storage of 1,1-dichloroethane and from 1,1,1-trichloroethane product storage. Handling emissions (source D) result from the loading of 1,1,1-trichloroethane into tank trucks or tank cars for shipment.

Fugitive emissions (E) occur when leaks develop in valves or compressor seals. When process pressures are higher than the cooling-water pressure, VOC can leak into the cooling water and escape as a fugitive emission from the cooling towers.

Secondary emissions can occur when wastewater from miscellaneous process sources (source F) is sent to a wastewater treatment system and the contained VOC are desorbed. Other sources of secondary emissions are from the disposal of catalyst residue (source G) in landfill and from the combustion of organic wastes (source H). (Secondary emissions occur when VOC are emitted with the combustion flue gas.)

3. Ethane Process

When chlorine is reacted with ethane, the main sequence of reactions occurring can be summarized as follows:[5]

$$\begin{array}{ccccccc}
CH_3\text{-}CH_3 & \xrightarrow[-HCl]{+Cl_2} & CH_3\text{-}CH_2Cl & \xrightarrow[-HCl]{+Cl_2} & CH_3\text{-}CHCl_2 & \xrightarrow[-HCl]{+Cl_2} & CH_3CCl_3 \\
\text{(ethane)} & & \text{(ethyl chloride)} & & \text{(1,1-dichloroethane)} & & \text{(1,1,1-trichloroethane)} \\
 & & -HCl & & -HCl & & -HCl \\
 & & CH_2{=}CH_2 & & CH_2{=}CHCl & & CH_2{=}CCl_2 \\
 & & \text{(ethylene)} & & \text{(vinyl chloride)} & & \text{(vinylidene chloride)}
\end{array}$$

Minor quantities of 1,2-dichloroethane and 1,1,2-trichloroethane are also produced. The product mix attained can be varied somewhat through changes in operating conditions. When 1,1,1-trichloroethane is the only desired product, the ethyl chlor and 1,1-dichloroethane produced are recycled to the chlorination reactor, and the vinyl chloride and vinylidene chloride are catalytically hydrochlorinated to 1,1-dichloroethane and 1,1,1-trichloroethane respectively, as represented by the following reactions:

$$\underset{\text{(vinyl chloride)}}{CH_2{=}CHCl} + HCl \xrightarrow{FeCl_3} \underset{\text{(1,1-dichloroethane)}}{CH_3{-}CHCl_2}$$

$$\underset{\text{(vinylidene chloride)}}{CH_2{=}CCl_2} + HCl \xrightarrow{FeCl_3} \underset{\text{(1,1,1-trichloroethane)}}{CH_3{-}CCl_3}$$

Figure III-2 represents a flow diagram for an ethane chlorination process.[5,6] For startup, ethane is circulated through the chlorination reactor and through a fuel-fired furnace (not shown) to bring the reactor temperature to about 350°C before normal feed flows are established. Chlorine (stream 1) and ethane (stream 2) supplied by pipeline are then fed to the reactor. The approximate chlorination reaction conditions are a temperature of 400°C and a pressure of 600 kPa. The reactor is operated adiabatically with a residence time of about 15 sec. A catalyst is not required for the chlorination reaction. When recycle flows are established, the 1,1-dichloroethane and ethyl chloride formed in the process (12 and 19) are also introduced as chlorination reactor feed.

The exit stream (3) from the reactor contains ethane, ethylene, vinyl chloride, ethyl chloride, vinylidene chloride, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,2-trichloroethane, 1,1,1-trichloroethane, a small amount of other chlorinated hydrocarbons, and hydrogen chloride.

The reactor effluent gas (stream 3) enters the quench column, where it is cooled and a residue stream consisting primarily of tetrachloroethane and hexachloroethane is removed (source H).

The overhead stream (4) from the quench column enters the hydrogen chloride column for separation of ethane, ethylene, and hydrogen chloride from the chlorinated hydrocarbons. A part of the hydrogen chloride column overhead stream (5) supplies the hydrogen chloride requirements of the hydrochlorination reactor. The excess hydrogen chloride and the contained ethane and ethylene (stream 6) pass to a hydrogen chloride purification step (not shown), eventually providing hydrogen chloride for other processes.

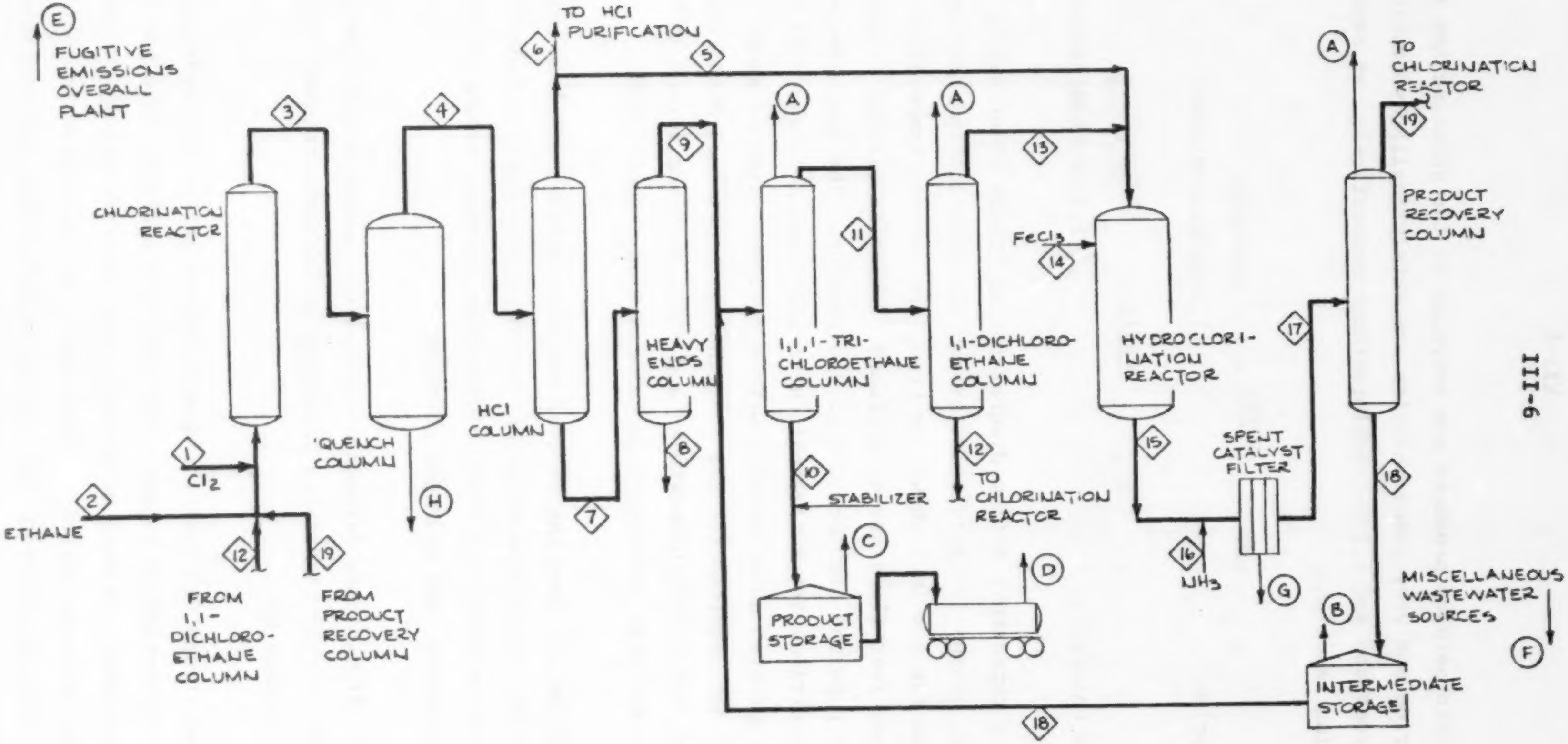
E
FUGITIVE EMISSIONS OVERALL PLANT
CHLORINATION REACTOR
1
Cl2
2
ETHANE
12
FROM 1,1-DICHLORO-ETHANE COLUMN
19
FROM PRODUCT RECOVERY COLUMN
3
'QUENCH COLUMN
H
4
HCl COLUMN
6
TO HCl PURIFICATION
5
7
HEAVY ENDS COLUMN
8
9
A
1,1,1-TRI-CHLOROETHANE COLUMN
10
STABILIZER
PRODUCT STORAGE
C
D
11
A
1,1-DICHLORO-ETHANE COLUMN
12
TO CHLORINATION REACTOR
13
FeCl3
14
HYDROCLORI-NATION REACTOR
15
16
NH3
SPENT CATALYST FILTER
G
17
A
TO CHLORINATION REACTOR
19
PRODUCT RECOVERY COLUMN
18
B
INTERMEDIATE STORAGE
18
MISCELLANEOUS WASTEWATER SOURCES
F

Fig. III-2. Flow Diagram for 1,1,1-Trichloroethane from Ethane

The hydrogen chloride—free chlorinated hydrocarbons (stream 7) from the hydrogen chloride column pass to the heavy-ends column, where the higher boiling components (primarily 1,2-dichloroethane and 1,1,2-trichloroethane) are removed as a bottoms stream (8) and are transferred as feed to other chlorinated hydrocarbon processes (e.g., perchloroethylene). The overhead stream (9), composed primarily of 1,1,1-trichloroethane, vinyl chloride, vinylidene chloride, ethyl chloride, and 1,1-dichloroethane, is combined with the bottoms stream (18) from the product recovery column and fed to the 1,1,1-trichloroethane column. Refined 1,1,1-trichloroethane is removed as the bottoms stream (10). After a stabilizer is added, the 1,1,1-trichloroethane is transferred to product storage.

The overhead stream (11) from the 1,1,1-trichloroethane column is fed to the 1,1-dichloroethane column, where 1,1-dichloroethane is separated as the bottoms stream (12) and is recycled as feed to the chlorination reactor. The overhead stream (13), composed of vinyl chloride, vinylidene chloride, and ethyl chloride, is fed to the hydrochlorination reactor, where vinyl chloride is converted to 1,1-dichloroethane and vinylidene chloride is converted to 1,1,1-trichloroethane. Hydrogen chloride requirements are supplied by a part of the hydrogen chloride column overhead stream (stream 5). Hydrochlorination reactor conditions include a temperature of 65°C, a pressure 450 kPa, and a catalytic amount of ferric chloride (stream 14).

Ammonia (stream 16) is added to the reactor effluent stream (stream 15) and reacts with the residual hydrogen chloride and ferric chloride to form a solid ammonium chloride—ferric chloride—ammonia complex. The solid complex is removed by the spent catalyst filter as a semisolid waste stream (source G). The filtered hydrocarbon stream (17) passes to the product recovery column, where a rough separation of 1,1,1-trichloroethane from the 1,1-dichloroethane—ethyl chloride fraction is made. The bottoms fraction (stream 18), composed primarily of 1,1,1-trichloroethane, is recycled to the 1,1,1-trichloroethane column. The overhead stream (19), consisting primarily of ethyl chloride and 1,1-dichloroethane, is recycled to the chlorination reactor.

The distillation column vents (A), which release primarily noncondensable gases, are the only significant source of process emissions. Storage emission sources (vents B and C) include intermediate storage and product storage. Handling emissions (vent D) result from the loading of 1,1,1-trichloroethane into tank cars and tank trucks.

Fugitive emissions (E) occur when leaks develop in valves or in pump seals. When process pressures are higher than the cooling-water pressure, VOC can leak into the cooling water and escape as a fugitive emission from the cooling towers.

Secondary emissions can occur when wastewater from miscellaneous process sources (source F) is sent to a wastewater treatment system and the contained VOC are desorbed. Other sources of secondary emissions are from the disposal of catalyst residue (source G) and from the combustion of liquid wastes (source H). (Secondary emissions occur when VOC are emitted with the combustion flue gas.)

C. PERCHLOROETHYLENE AND TRICHLOROETHYLENE

1. Introduction

Perchloroethylene and trichloroethylene are produced separately or as co-products by either chlorination or oxychlorination of ethylene dichloride or other C_2 chlorinated hydrocarbons, with the raw-material ratios determining the proportions of perchloroethylene and trichloroethylene.[1] Of the domestic plants using the chlorination process, one produces only perchloroethylene,[7] a second produces only trichloroethylene,[8] and a third produces both perchloroethylene and trichloroethylene as co-products.[9] Perchloroethylene and trichloroethylene are also produced as co-products by the one plant that uses the oxychlorination process.[3] Perchloroethylene and carbon tetrachloride are produced as co-products by the chlorinolysis of hydrocarbons and their partially chlorinated derivatives. This process produces more perchloroethylene than do the other processes combined and is described in a previous product report.[10]

2. Chlorination

The main reactions for the chlorination of ethylene dichloride to perchloroethylene and trichloroethylene are as follows:

$ClCH_2CH_2Cl$	+	$3\ Cl_2$	$\longrightarrow$	$Cl_2C{=}CCl_2$	+	$4HCl$
(ethylene dichloride)		(chlorine)		(perchloroethylene)		(hydrogen chloride)

$ClCH_2CH_2Cl$	+	$2Cl_2$	$\longrightarrow$	$Cl_2C{=}CHCl$	+	$3HCl$
(ethylene dichloride)		(chlorine)		(trichloroethylene)		(hydrogen chloride)

The chlorination is carried out at a high temperature (400 to 450°C), slightly above atmospheric pressure, and without the use of a catalyst. Other chlorinated C_2 hydrocarbons or recycled chlorinated hydrocarbon by-products may be fed to the chlorinator. The large quantity of hydrogen chloride produced is usually used in other processes.[1]

The flow diagram shown in Fig. III-3 represents a process for chlorinating ethylene dichloride and other C_2 chlorinated organics to make perchloroethylene and trichloroethylene. Ethylene dichloride (stream 1) and chlorine (stream 2) are fed to the reactor and quench area, where they are first vaporized and then sent to the reactor. Hydrogen chloride (stream 3) is separated from the chlorinated hydrocarbon mixture (stream 4) produced in the reactor and sent to other processes. The chlorinated hydrocarbon mixture (stream 4) is neutralized with sodium hydroxide solution (stream 5), which leaves the system as wastewater (F) when spent, and is then dried.[7]

The dried crude product (stream 7) is separated by the perchloroethylene/trichloroethylene column into crude trichloroethylene (stream 8) and crude perchloroethylene (stream 9). The crude trichloroethylene (stream 8) goes to the trichloroethylene column, where the lights (stream 10) go overhead and the bottoms (stream 11), containing trichloroethylene and heavies, are sent to the finishing column. Trichloroethylene (stream 12) is taken overhead and sent to trichloroethylene storage; the heavies (stream 13) are combined with the lights (stream 10) from the trichloroethylene column and sent to the recycle organic storage.[7,9]

The crude perchloroethylene (stream 9) from the perchloroethylene/trichloroethylene column is separated in the perchloroethylene column; the perchloroethylene (stream 14) goes overhead to perchloroethylene storage and the bottoms (stream 15) go to the heavies column. There the heavies (stream 16) go overhead and are sent to the recycle organic storage. The tars (G) are sent to an incinerator for disposal.[7—9]

If any C_2 chlorinated organics (stream 18) from other processes are fed to the process, they may be combined with the recycled lights and heavies (streams 10, 13, and 16) and the combined recycle organics (stream 19) fed to the reactor and quench area.[7—9]

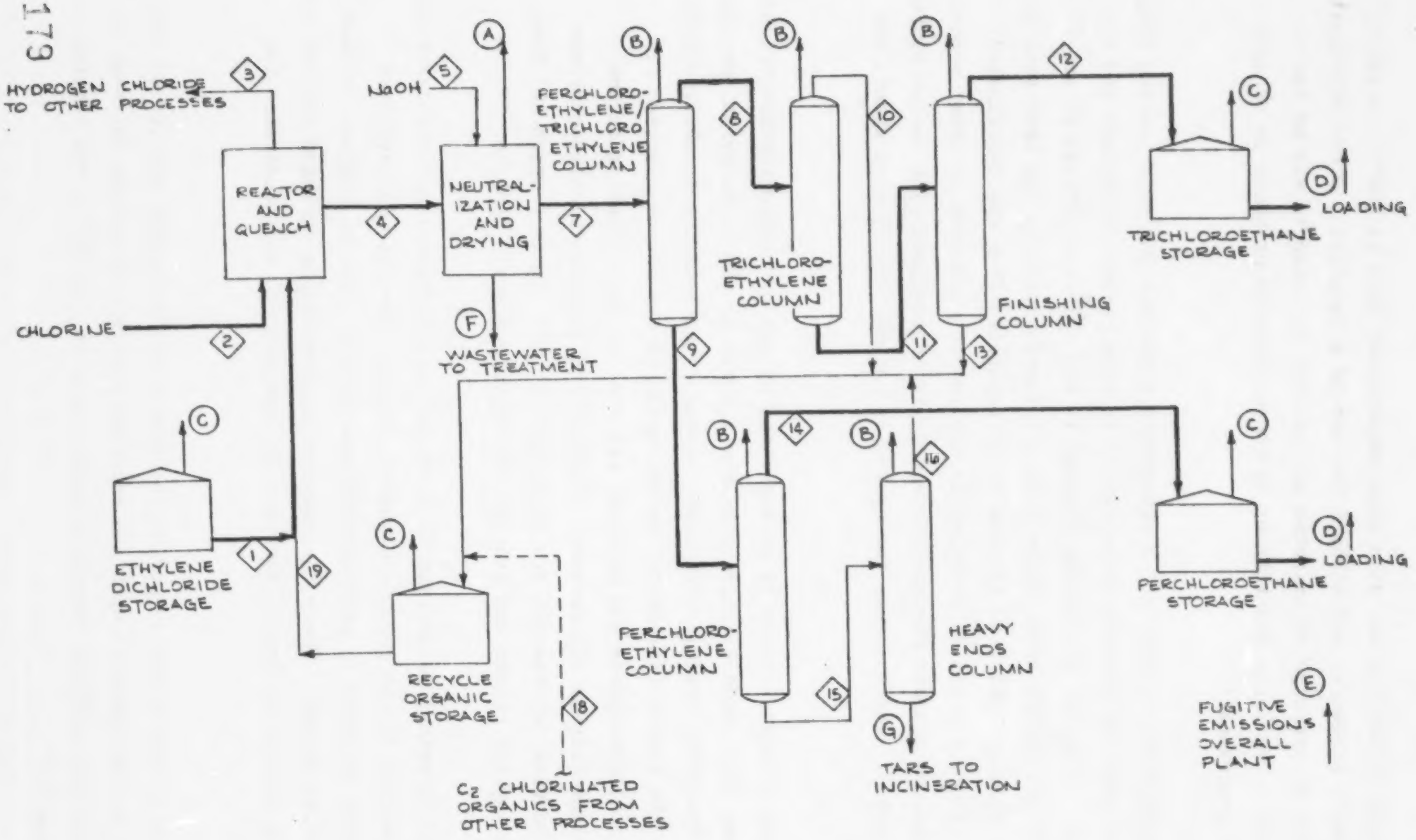
HYDROGEN CHLORIDE TO OTHER PROCESSES
3
REACTOR AND QUENCH
CHLORINE
2
4
NaOH
5
A
NEUTRALIZATION AND DRYING
7
F
WASTEWATER TO TREATMENT
B
PERCHLORO-ETHYLENE/TRICHLORO ETHYLENE COLUMN
8
9
B
TRICHLORO-ETHYLENE COLUMN
10
11
B
FINISHING COLUMN
12
13
C
TRICHLOROETHANE STORAGE
D
LOADING
C
ETHYLENE DICHLORIDE STORAGE
1
19
C
RECYCLE ORGANIC STORAGE
18
C2 CHLORINATED ORGANICS FROM OTHER PROCESSES
B
14
PERCHLORO-ETHYLENE COLUMN
15
B
16
HEAVY ENDS COLUMN
G
TARS TO INCINERATION
C
PERCHLOROETHANE STORAGE
D
LOADING
E
FUGITIVE EMISSIONS OVERALL PLANT

Fig. III-3. Flow Diagram for Perchloroethylene and Trichloroethylene by Chlorination

The neutralization and drying area vent (A), which releases the inert gases from the chlorine and ethylene dichloride feeds, and the distillation column vents (B), which release primarily noncondensable gases, are sources of process emissions. Storage emission sources (vents C) are raw-material storage, recycle storage, and product storage. Handling emissions (vents D) can occur while perchloroethylene and trichloroethylene are being loaded into drums, tank trucks, tank cars, barges, or ships for shipment.[7—9]

Fugitive emissions (E) occur when leaks develop in valves or in pump seals. When process pressures are higher than the cooling-water pressure, VOC can leak into the cooling water and escape as a fugitive emission from the cooling tower.

Secondary emissions can occur when wastewater containing VOC is sent to a wastewater treatment system or lagoon and the VOC are desorbed (F). Another source of secondary emissions is the combustion of tars in an incinerator where VOC are emitted with the flue gases (G).[7]

3. Oxychlorination[3,11,12]

The main reactions for the oxychlorination of ethylene dichloride to perchloroethylene and trichloroethylene are as follows:

$$\underset{\text{(ethylene dichloride)}}{ClCH_2CH_2Cl} + \underset{\text{(chlorine)}}{Cl_2} + \underset{\text{(oxygen)}}{O_2} \xrightarrow{CuCl_2} \underset{\text{(perchloroethylene)}}{Cl_2C{=}CCl_2} + \underset{\text{(water)}}{2H_2O}$$

$$\underset{\text{(ethylene dichloride)}}{4ClCH_2CH_2Cl} + \underset{\text{(chlorine)}}{2Cl_2} + \underset{\text{(oxygen)}}{O_2} \xrightarrow{CuCl_2} \underset{\text{(trichloroethylene)}}{4Cl_2C{=}CHCl} + \underset{\text{(water)}}{6H_2O}$$

Hydrogen chloride and chlorinated organics may be fed to supply the chlorine, either in combination with chlorine or separately. Side reactions produce carbon dioxide, hydrogen chloride, and several chlorinated hydrocarbons. A fluid-bed reactor containing a vertical bundle of tubes with boiling liquid outside the tubes is used to control the reaction temperature at about 425°C. The reactor is operated at pressures slightly above atmospheric, and the catalyst, which contains copper chloride, is continuously added to the tube bundle as entrained catalyst fines are carried away with the crude product. The crude product contains 85 to 90 wt % perchloroethylene plus trichloroethylene and 10 to 15 wt % by-product organics. Essentially all by-product organics are recovered during purification and are recycled to the reactor. The process is very flexible, so that the reaction can be directed toward the production of either perchloroethylene or trichloroethylene in varying proportions.

The flow diagram shown in Fig. III-4 is based on information provided by PPG;[3] data on this process are also given in the literature.[11,12] Ethylene dichloride (stream 1), chlorine or hydrogen chloride (stream 2), and oxygen (stream 3) are fed to the fluid-bed reactor as gases.[6] Catalyst fines generated by the fluidization of the catalyst in the reactor leave with the gaseous product (stream 4). The reactor product is condensed in both a water-cooled condenser and a refrigerated condenser; all the condensed material and the catalyst fines drain to a decanter. The noncondensed inert gases (stream 5), consisting of carbon dioxide, hydrogen chloride, nitrogen, and a small amount of uncondensed chlorinated hydrocarbons, go to the hydrogen chloride absorber, where hydrogen chloride is recovered by absorption in process water to make by-product hydrochloric acid and the remaining inert gases are purged (vent A).

In the decanter the crude product (stream 7) is phase-separated from the aqueous phase and catalyst fines (stream 8), which goes to waste treatment (H), and then the crude product is sent to the drying column for removal of dissolved water by azeotropic distillation. The water (stream 9) from the drying column goes to waste treatment (H) and the dried crude product (stream 10) is separated into crude trichloroethylene (stream 11) and crude perchloroethylene (stream 12) in the perchloroethylene/trichloroethylene column.

The crude trichloroethylene (stream 11) is sent to the trichloroethylene column, where the lights (stream 13) go overhead and are sent to the recycle organic storage. The bottoms (stream 14) are neutralized with ammonia in the trichloroethylene neutralizer and then dried in the trichloroethylene dryer to obtain the finished trichloroethylene (stream 15) that is sent to the trichloroethylene storage.

The crude perchloroethylene (stream 12) from the perchloroethylene/trichloroethylene column goes to the heavies column, where perchloroethylene and lights (stream 16) go overhead to the perchloroethylene column and the heavies (stream 17) remaining

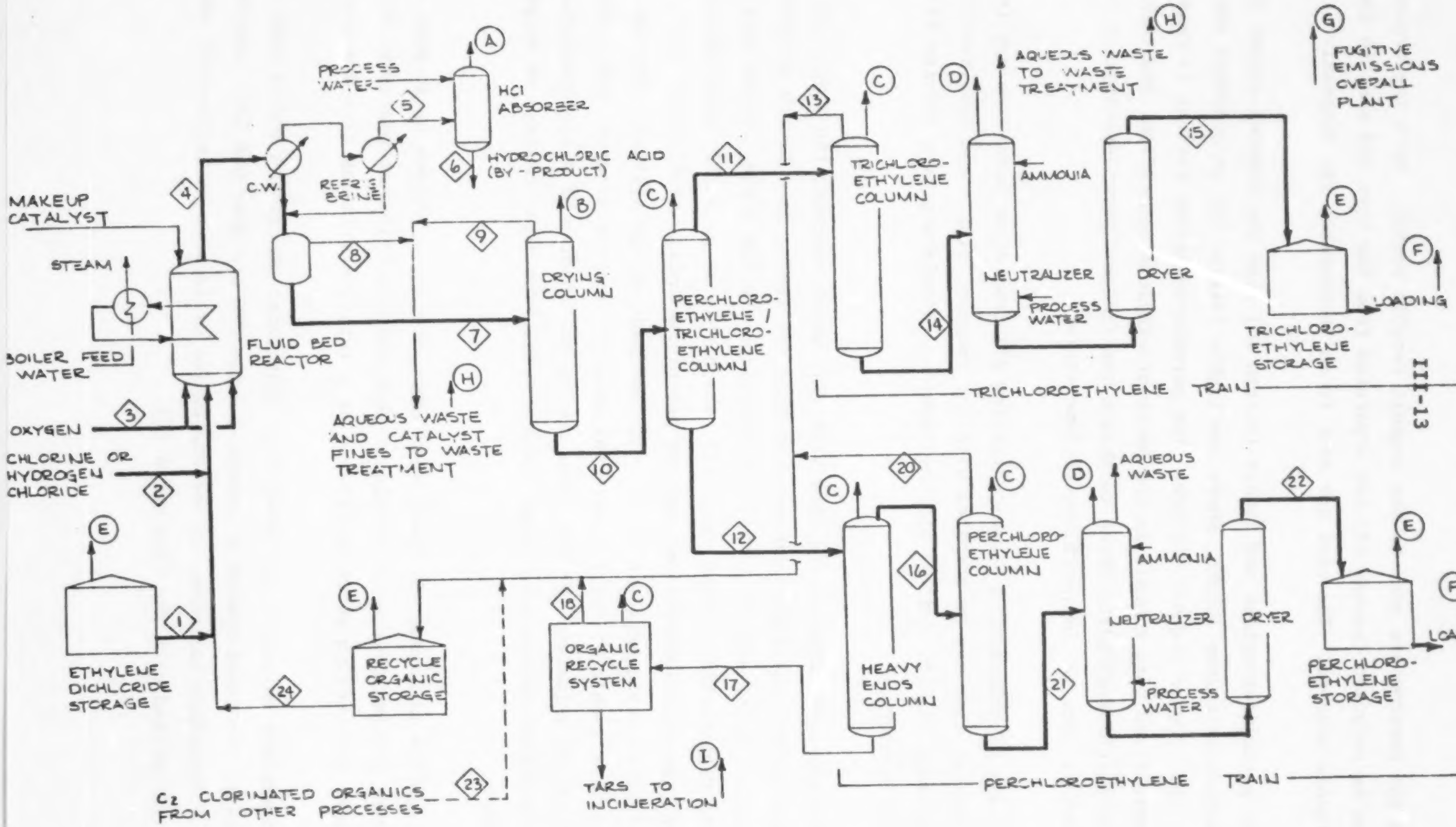
MAKEUP CATALYST
STEAM
BOILER FEED WATER
OXYGEN
CHLORINE OR HYDROGEN CHLORIDE
ETHYLENE DICHLORIDE STORAGE
FLUID BED REACTOR
C.W.
REFRIG BRINE
PROCESS WATER
HCl ABSORBER
HYDROCHLORIC ACID (BY-PRODUCT)
AQUEOUS WASTE AND CATALYST FINES TO WASTE TREATMENT
DRYING COLUMN
PERCHLORO-ETHYLENE / TRICHLORO-ETHYLENE COLUMN
TRICHLORO-ETHYLENE COLUMN
NEUTRALIZER
AMMONIA
PROCESS WATER
DRYER
AQUEOUS WASTE TO WASTE TREATMENT
TRICHLORO-ETHYLENE STORAGE
LOADING
FUGITIVE EMISSIONS OVERALL PLANT
TRICHLOROETHYLENE TRAIN
RECYCLE ORGANIC STORAGE
ORGANIC RECYCLE SYSTEM
TARS TO INCINERATION
C2 CLORINATED ORGANICS FROM OTHER PROCESSES
HEAVY ENDS COLUMN
PERCHLORO-ETHYLENE COLUMN
NEUTRALIZER
AMMONIA
PROCESS WATER
AQUEOUS WASTE
DRYER
PERCHLORO-ETHYLENE STORAGE
LOADING
PERCHLOROETHYLENE TRAIN
A
B
C
D
E
F
G
H
I
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
20
21
22
23
24

Fig III-4. Flow Diagram for Perchloroethylene and Trichloroethylene by Oxychlorination

as the bottoms are sent to the organic recycle system. Here the organics that can be recycled (stream 18) are separated from the tars and sent to the recycle organic storage. The tars are sent to an incinerator for disposal.

The perchloroethylene and lights (stream 16) from the heavies column go to the perchloroethylene column, where the lights (stream 20) go overhead and are sent to the recycle organic storage. The perchloroethylene bottoms (stream 21) are neutralized with ammonia in the perchloroethylene neutralizer and then dried in the perchloroethylene dryer to obtain the finished perchloroethylene (stream 22) that is sent to the perchloroethylene storage.

If any C_2 chlorinated organics (stream 23) from other processes are fed to the process, they may be combined with the recycled lights and recovered organics (streams 13, 18, and 20) and the combined recycle organics (stream 24) fed to the reactor.

The hydrogen chloride absorber vent (A), which releases the inert gases from the oxygen, chlorine, and hydrogen chloride feeds, is a source of process emissions. Other sources of process emissions are the drying column vent (B) and the distillation column vents (C), which release primarily noncondensable gases, and the trichloroethylene and the perchloroethylene neutralizer vents (D), which relieve excess pressure of the nitrogen pads on the systems. Storage emisson sources (vents E) are raw material storage, recycle storage, and product storage. Handling emissions (F) can occur during the loading of perchloroethylene and trichloroethylene into drums, tank trucks, tank cars, barges, or ships for shipment.

Fugitive emissions (G) occur when leaks develop in valves or in pump seals. When process pressures are higher than the cooling-water pressure, VOC can leak into the cooling water and escape as a fugitive emission from the cooling tower.

Secondary emissions can occur when wastewater containing VOC is sent to a wastewater treatment system or lagoon and the VOC are desorbed (H). Another source of secondary emissions is the combustion of tars in an incinerator where VOC are emitted with the flue gases (I).

D. VINYLIDENE CHLORIDE

Vinylidene chloride is produced domestically by the dehydrochlorination of 1,1,2-trichloroethane as represented by the following reaction:[8,13,14]

$$\underset{\text{(1,1,2-trichloroethane)}}{CH_2Cl\text{-}CHCl_2} + \underset{\text{(sodium hydroxide)}}{NaOH} \longrightarrow \underset{\text{(vinylidene chloride)}}{CH_2{=}CCl_2} + \underset{\text{(sodium chloride)}}{NaCl} + \underset{\text{(water)}}{H_2O}$$

The reaction is carried out in the liquid phase at a temperature of about 100°C, with a relatively dilute (5 to 10 wt %) sodium hydroxide solution. Product yields are believed to range from 85 to 90%.[13]

Figure III-5 represents a flow diagram for a process in which vinylidene chloride is produced from 1,1,2-trichloroethane.[8,13,14] Concentrated sodium hydroxide solution (stream 1) is diluted with water (stream 2) to 5 to 10% concentration and combined with 1,1,2-trichloroethane feed (stream 3), with unreacted 1,1,2-trichloroethane (stream 16) recycled from the distillation section of the process, and with a recycled sodium hydroxide—salt solution (stream 8). The combined feed stream (4) is further mixed to provide dispersal of the insoluble organic phase in the aqueous phase before it is fed to the dehydrochlorination reactor. The dehydrochlorination reactor is continuously purged with nitrogen (stream 5) to prevent the accumulation of monochloroacetylene impurity in the vinylidene chloride product, a step that results in a process emission source (vent A).

The two-phase reactor effluent (stream 6) is separated into two streams. The aqueous phase (stream 7), composed of a sodium hydroxide—salt solution saturated with organic compounds, is split. One fraction (stream 8) is recycled to the dehydrochlorination reactor. The other fraction (stream 9) is combined with the bottom stream (14) from the drying column and fed to the stripping column, where steam (10) is introduced countercurrently to strip most of the dissolved organics from the aqueous phase. The organics (stream 11) are removed overhead and are combined with the organic phase (stream 12) from the phase separator as feed to the drying column. The stripped aqueous phase is removed as the bottom stream (source F) and discharged to the wastewater treatment system.

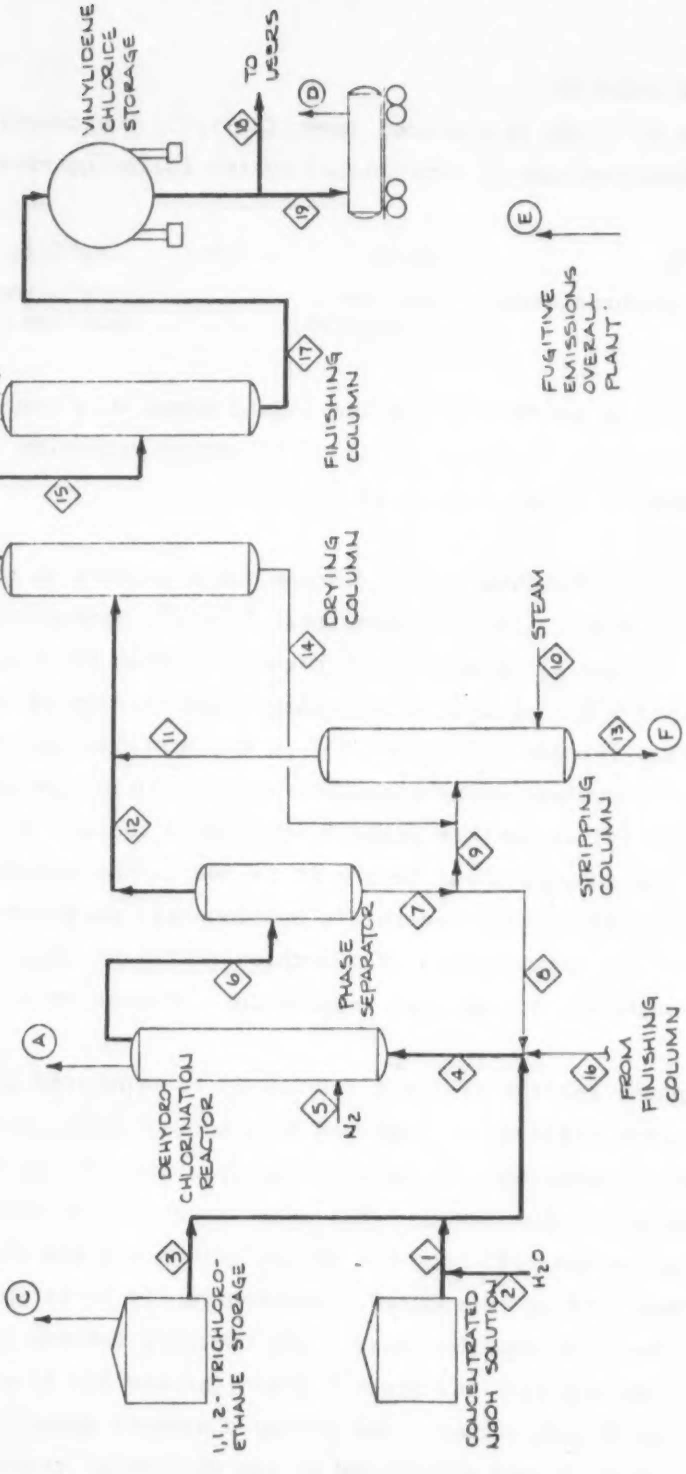
VINYLIDENE CHLORIDE STORAGE
TO USERS
18
D
19
E
FUGITIVE EMISSIONS OVERALL PLANT
TO REACTOR
16
B
17
FINISHING COLUMN
15
B
DRYING COLUMN
14
STEAM
10
11
13
F
STRIPPING COLUMN
12
9
7
PHASE SEPARATOR
6
8
A
DEHYDRO-CHLORINATION REACTOR
5
N_2
4
16
FROM FINISHING COLUMN
3
C
1,1,2-TRICHLORO-ETHANE STORAGE
1
2
H_2O
CONCENTRATED NaOH SOLUTION

Fig. III-5. Flow Diagram for Vinylidene Chloride from 1,1,2-Trichloroethane

The drying column bottom stream (14), which contains most of the residual water, is recycled to the stripping column. The drying-column overhead stream (15) passes to the finishing column, where the overhead stream (16), composed primarily of unreacted 1,1,2-trichloroethane, is removed and recycled to the dehydrochlorination reactor. The refined vinylidene chloride product is removed as the bottom stream (17) and transferred to storage in pressurized tanks. From storage the vinylidene chloride may be transferred by pipeline for internal use (stream 18) or loaded (stream 19) into tank trucks and tank cars for off-site consumption.

The dehydrochlorination reactor purge vent (A) and the distillation column vents, (B) which release primarily noncondensable gases, are sources of process emissions. Storage emissions (vent C) are the emissions from storage of 1,1,2-trichloroethane. Handling emissions (vent D) result from the loading of vinylidene chloride into tank trucks and railroad tank cars. With pressurized tanks used for vinylidene chloride storage no significant emissions from product storage occur.

Fugitive emissions (E) occur when leaks develop in valves or in pump or compressor seals. When process pressures are higher than the cooling water pressure, VOC can leak into the cooling water and escape as fugitive emissions from the cooling tower.

Secondary emissions can occur when wastewater discharged from the stripping column (source F) is sent to a wastewater treatment system and the contained VOC are desorbed.

E. REFERENCES*

1. S. A. Cogswell, "C_2 Chlorinated Solvents," pp. 632.3000A—F and 632.3001A—632.3002A in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (December 1978).

2. "1,1,1-Trichloroethane," p 9 in Chemical Marketing Reporter (Jan. 17, 1977).

3. F. C. Dehn, PPG Industries, Inc., letter dated Mar. 14, 1979, to EPA with information on air emissions from the 1,1,1-trichloroethane plant and the perchloroethylene and trichloroethylene plant at Lake Charles, LA, in response to EPA request.

4. T. A. Leonard, Vulcan Materials Company, letter dated Mar. 8, 1979, to EPA with information on air emissions from the 1,1,1-trichloroethane plant at Geismar, LA, in response to EPA request.

5. Z. S. Khan and T. W. Hughes, Monsanto Research Corporation, Source Assessment: Chlorinated Hydrocarbons Manufacture, June 1977 (preliminary draft on file at EPA, ESED, Research Triangle Park, NC).

6. L. M. Elkin, Chlorinated Solvents, Report 48, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (February 1969).

7. J. B. Worthington, Diamond Shamrock, letter dated Jan. 16, 1979, to EPA with information on air emissions from the perchloroethylene plant at Deer Park, TX, in response to EPA request.

8. R. L. Standifer, IT Enviroscience, Inc., Trip Report for Visit to Dow Chemical USA, Freeport, TX, Nov. 9, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

9. W. C. Strader, Ethyl Corporation, letter dated Nov. 28, 1978, to EPA with information on air emissions from the perchloroethylene and trichloroethylene plant at Baton Rouge, LA, in response to EPA request.

10. F. D. Hobbs and C. W. Stuewe, IT Enviroscience, Inc., Carbon Tetrachloride and Perchloroethylene (Hydrocarbon Chlorinolysis Process) (in preparation for EPA, ESED, Research Triangle Park, NC).

11. "PPG Industries: Chlorinated Solvents from Ethylene," Chemical Engineering 76(26), 90, 91 (1969).

12. J. F. Knoop and G. R. Neikirk, "Oxychlorinate for Per/Tri," Hydrocarbon Processing 51 (11), 109, 110 (1972).

13. Arthur D. Little, Inc., Final Report: Vinylidene Chloride Monomer Emissions from the Monomer, Polymer, and Polymer Processing Industries, ADR-76086-31, prepared for the EPA Control Systems Laboratory, Durham, NC (April 1976).

14. J. Beale, Dow Chemical Co. USA, letter dated Oct. 25, 1978, to EPA with information on air emissions from the vinylidene chloride plant at Plaquemine, LA, in response to EPA request.

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS

A. INTRODUCTION

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. A relatively small number of organic chemicals are photochemically unreactive. It should be noted that although 1,1,1-trichloroethane is included in VOC emission totals in this report, it does not, based on current research data, participate in ozone-forming reactions to an appreciable extent. However, many photochemically unreactive organic chemicals are of concern and may not be exempt from regulation by EPA under Section 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation.

B. 1,1,1-TRICHLOROETHANE

1. Vinyl Chloride Process

a. Model Plant*——The model plant for the synthesis of 1,1,1-trichloroethane from vinyl chloride (Fig. III-1) has a capacity of 136,000 Mg/yr based on 8760 hr of operation annually.** This capacity is typical of recently built plants that manufacture 1,1,1-trichloroethane from vinyl chloride.[1—4] Information about the specific process steps and the sequence of specific operations for existing plants was not available; however, the process shown in Fig. III-1 is believed to be similar to the actual processes used. Characteristics of the model plant important to air-dispersion modeling are shown in Table B-1 in Appendix B.

b. Sources and Emissions——Uncontrolled emission sources and rates for the vinyl chloride—based 1,1,1-trichloroethane process are summarized in Table IV-1.

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*See p I-2 for a discussion of model plants.

**Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and the annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation is negligible.

Table IV-1. Estimates of Total Uncontrolled VOC Emissions from a Model Plant Producing 1,1,1-Trichloroethane from Vinyl Chloride (136,000 Mg/yr)[a]

Source	Vent Designation (Fig.III-1)	VOC Emissions Ratio (g/kg)[b]	VOC Emissions Rate (kg/hr)
Distillation vents	A	0.19	3.0
Storage vents			
Intermediate storage	B	0.15[c]	2.3
Product storage	C	0.40[d]	6.2
Handling—loading tank trucks and tank cars	D	0.61	9.5
Fugitive	E	1.26	19.5
Secondary			
Wastewater treatment	F	0.001	0.02
Incineration of residues and/or landfill	G,H	<0.001	<0.01
Total		2.6	40.5

[a] Uncontrolled emissions are emissions from a process for which there are no control devices other than those necessary for economical operation.

[b] g of emissions per kg of 1,1,1-trichloroethane produced.

[c] Includes approximately 60% nonreactive VOC (1,1,1-trichloroethane).

[d] Primarily nonreactive VOC (1,1,1-trichloroethane).

Distillation vent——The gas vented from the distillation columns reflux condensers (vents A, Fig. III-1), primarily noncondensable nitrogen and oxygen, is the only significant source of process emissions. The estimated composition of the uncontrolled distillation vent gas, shown in Table IV-2, is based on a reported composition after the use of a control device[5] and on an estimated VOC removal efficiency of 90% for the control.[6]

Storage and handling emissions——Emissions result from intermediate process storage and from the storage of refined 1,1,1-trichloroethane. Sources for the model plant are shown in Fig. III-1 (sources B and C). Storage tank data for the model plant are given in Table IV-3. The uncontrolled storage emissions were calculated by the use of the emission equations from AP-42,[7] and are based on fixed-roof tanks, half full, with a diurnal temperature variation of 11°C. The calculated values for breathing losses were divided by 4 to account for recent evidence that the AP-42 breathing-loss equation overpredicts emissions. Handling emissions result from the loading (source D) of 1,1,1-trichloroethane into tank cars and tank trucks for shipment. These emissions are shown in Table IV-1 and were calculated with the equations from AP-42,[7] based on the submerged loading of 1,1,1-trichloroethane at 27°C and with all the production being shipped in tank cars and tank trucks. Storage and handling emissions, the most significant source of emissions from the model plant, account for about 75% of the uncontrolled emissions.

Fugitive emissions——Process pumps, compressors, process valves, and pressure-relief devices are potential sources of fugitive emissions (source E). The model plant is estimated to have 30 pumps, 2 compressors (with 2 seals), 1000 process valves, and 15 pressure-relief devices handling VOC. The actual number of each component used in existing 1,1,1-trichloroethane plants was not available; therefore they were estimated based on the average numbers of components in service in plants producing chloromethanes.[8] Pumps, compressors, process valves, and pressure-relief valves not handling VOC are not included in these estimates. The fugitive emission factors from Appendix C were applied to these estimates, and the results are shown in Table IV-1 as fugitive emissions.

Secondary emissions——Secondary VOC emissions can result from the handling and disposal of process waste streams. For the model plant three potential sources are indicated on the flow diagram (sources F, G and H).

Table IV-2. Estimated Composition of Distillation Vent Gas from Model Plant Producing 1,1,1-Trichloroethane from Vinyl Chloride*

Component	Composition (wt %)
Vinyl chloride	0.1
Ethylene dichloride	2.5
Total VOC	2.6
Oxygen, nitrogen	97.3
Carbon dioxide	0.1
Total	100.0

*See refs 5 and 6.

Table IV-3. Storage Tank Data for 1,1,1-Trichloroethane (Vinyl Chloride Feed) Model Plant

	Tank		
	Intermediate	Intermediate	Product
Contents	Crude 1,1-dichloroethane	Crude 1,1,1-trichloroethane	Refined 1,1,1-trichloroethane
Number of tanks	3	2	4
Tank size (m^3)	189	98	598
Turnovers per year	13	52	86
Bulk temperature (°C)	27	27	27

The estimate of secondary emissions from wastewater treatment (source F) for the model plant is based on steam-stripping of all wastewater containing VOC for recovery of the contained organics before the water is discharged to the wastewater treatment system.[4] Emissions from wastewater treatment and landfill of residues will be discussed in a future EPA report on secondary emissions.

The venting of flue gas produced from the combustion of liquid residues (source H) in an incinerator results in the secondary emission of VOC. Specific information as to the quantity and composition of the residues that are burned was not available, however, estimates previously made for similar processes[9,10] indicate that emissions from this source are characteristically low, as are emissions resulting from the landfill of solid residues (G). The estimated emissions shown in Table IV-1 are based on the previous estimates.

2. Ethane Process

a. Model Plant——The model plant for the synthesis of 1,1,1-trichloroethane from ethane (Fig. III-2) has a capacity of 29,500 Mg/yr based on 8760 hr of operation annually. This is the reported capacity of the Vulcan Materials Company plant at Geismar, LA, the only plant currently using the ethane process for the manufacture of 1,1,1-trichloroethane.[3,11] Information concerning specific process steps and the sequence of specific operations was not available for the Vulcan process. The flow diagram for the model plant (Fig. III-2) was based primarily on information obtained from general references[12,13] and does not specifically represent the process used by Vulcan. Characteristics of the model plant important to air-dispersion modeling are shown in Table B-2 in Appendix B.

b. Sources and Emissions——Emission sources and rates for the ethane-based 1,1,1-trichloroethane process are summarized in Table IV-4.

Distillation vents——The gas vented from the distillation-column reflux condenser vents (A, Fig. III-2) is the only significant source of process emissions. The estimated composition of the uncontrolled distillation vent gas is shown in Table IV-5.

Table IV-4. Estimates of Total Uncontrolled VOC Emissions from a Model Plant Producing 1,1,1-Trichloroethane from Ethane (29,500 Mg/yr)[a]

Source	Vent Designation (Fig.III-2)	VOC Emissions Ratio (g/kg)[b]	VOC Emissions Rate (kg/hr)
Distillation vents	A	0.21[c]	0.7
Storage vents			
Recycle storage	B	0.15[d]	0.5
Product storage	C	0.40[e]	1.4
Handling	D	0.61	2.1
Fugitive	E	5.79	19.5
Secondary			
Wastewater treatment	F	0.001	0.004
Incineration of residues and/or landfill	G,H	<0.003	<0.01
Total		7.2	24.2

[a] Uncontrolled emissions are emissions from a process for which there are no control devices other than those necessary for economical operation.

[b] g of emission per kg of 1,1,1-trichloroethane produced.

[c] Includes approximately 65% nonreactive VOC (1,1,1-trichloroethane).

[d] Includes approximately 60% nonreactive VOC (1,1,1-trichloroethane).

[e] Primarily nonreactive VOC (1,1,1-trichloroethane).

Table IV-5. Estimated Composition of Distillation Vent Gas from Model Plant Producing 1,1,1-Trichloroethane from Ethane*

Component	Composition (wt %)
1,1,1-Trichloroethane	35
Ethylene dichloride	17
Nitrogen, oxygen	48
Total	100

*See ref 10.

Storage and handling emissions——Emissions result from intermediate process storage and from the storage or handling of refined 1,1,1-trichloroethane. Sources for the model plant are shown in Fig. III-2 (sources B, C, and D). Specific storage requirements for the ethane-based 1,1,1-trichloroethane process were not available.

Storage and handling emissions result primarily from the storage and handling of 1,1,1-trichloroethane. As the corresponding emissions are primarily dependent on plant capacity and throughput and are not significantly affected by the process used, the estimated storage and handling emissions for the ethane-based 1,1,1-trichloroethane model plant given in Table IV-4 were developed by prorating the storage and throughput data for the vinyl-chloride—based 1,1,1-trichloroethane model plant (Table IV-3) to those for the smaller ethane-based model plant (see Table IV-6).

Fugitive emissions——Process pumps, compressors, process valves, and pressure relief devices are potential sources (E) of fugitive emissions. The model plant is estimated to have 30 pumps, 2 compressors (with 2 seals), 1000 process valves, and 15 pressure-relief devices handling VOC. Since the actual number of each component used in the existing 1,1,1-trichloroethane plant was not available, they were estimated based on the average numbers of components in service in plants producing cloromethanes.[8] Pumps, compressors, and valves not handling VOC are not included in these estimates. The fugitive emission factors from Appendix C were applied to these estimates and the results are shown in Table IV-4 as fugitive emissions.

Secondary emissions——Secondary VOC emissions can result from the handling and disposal of process waste streams. For the model plant three potential sources (F, G, and H) are indicated on Fig. III-2.

The estimate of secondary emissions from wastewater treatment (source F) for the model plant is based on steam-stripping of all wastewater containing VOC for recovery of the contained organics before the water is discharged to the wastewater treatment system. Emissions from wastewater will be discussed in a future EPA report on secondary emissions.

Table IV-6. Storage Tank Data for 1,1,1-Trichloroethane (Ethane Feed) Model Plant

	Tank		
	Intermediate	Intermediate	Product
Contents	1,1-Dichloroethane	Crude 1,1,1-trichloroethane	Refined 1,1,1-trichloroethane
Number of tanks	4	2	4
Tank size (m^3)	55	29	174
Turnovers per year	11	44	73
Bulk temperature (°C)	27	27	27

The venting of flue gas produced from the combustion of liquid and semisolid residues in an incinerator results in the secondary emissions of VOC. Specific information as to the quantity and compostion of the residues that are burned was not available; however, estimates previously made for similar processes[9,10] indicate that emissions from this source are characteristically low. The estimated emissions shown in Table IV-4 are based on the previous estimates.

C. PERCHLOROETHYLENE AND TRICHLOROETHYLENE

1. Chlorination

The flow diagram shown in Fig. III-3 was based on information from producers of perchloroethylene and trichloroethylene[5,13,14] and on general engineering judgement. Because some details of the processes are considered to be confidential or were not given, the actual processes used may differ from those shown. A capacity of 70,000 Mg/yr based on 8760 hr of operation per year was chosen as being most representative of the three plants that produce perchloroethylene and/or trichloroethylene by chlorination of ethylene dichloride.

The estimate of the uncontrolled process emissions given in Table IV-7 does not include uncontrolled storage, handling, fugitive, or secondary emissions. The estimate is based on a weighted average of uncontrolled process emissions reported by perchloroethylene and trichloroethylene producers.[5,14,15] Storage, handling, fugitive, and secondary emissions for the entire synthetic organic chemicals manufacturing industry are covered by separate EPA documents.

The composition and flow of the gas from a neutralization and drying area vent (A), based on data from one producer, are given in Table IV-8, and similar data on the distillation vent (B) are given in Table IV-9.[14]

2. Oxychlorination

The flow diagram shown in Fig. III-4 represents a plant producing perchloroethylene and trichloroethylene by the oxychlorination process with a capacity of 180,000 Mg/yr based on 8760 hr of operation per year. It is based on the literature and on information from the one producer of perchloroethylene and trichloroethylene who uses this process. The estimate of the uncontrolled process emissions given in Table IV-7

Table IV-7. Estimates of Uncontrolled Process VOC Emissions from Processes Producing Perchloroethylene, Trichloroethylene, and Vinylidene Chloride

			VOC Emissions[a]	
Process	Product	Capacity (Mg/yr)	Ratio (g/kg)[b]	Rate (kg/hr)
Chlorination	Perchloroethylene and/or trichloroethylene	70,000	8	64
Oxychlorination	Perchloroethylene and trichloroethylene	180,000	24	500
Dehydrochlorination	Vinylidene chloride	90,000	8	82

[a] Storage, handling, fugitive, and secondary emissions are not included in these data.

[b] g of emission per kg of product produced.

Table IV-8. Estimated Composition of Neutralization and Drying Vent Gas from a Perchloroethylene Plant[a]

Component	Composition (wt %)	Emission Ratio[b] (g/kg)
Ethylene dichloride	30.5	3.1
Vinylidene chloride	25.1	2.5
trans-Dichloroethylene	10.9	1.1
cis-Dichloroethylene	2.91	0.29
Carbon tetrachloride	0.64	0.064
Trichloroethylene	1.08	0.11
Perchloroethylene	4.99	0.50
Total VOC	76	7.6
Water	0.02	0.002
Air	24	2.4
Total	100	10

[a] See ref 14.

[b] g of emission per kg of perchloroethylene produced.

Table IV-9. Estimated Composition of Distillation Vent Gas from a Perchloroethylene Plant[a]

Component	Composition (wt %)	Emission Ratio (g/kg)[b]
Vinylidene chloride	10.6	0.106
trans-Dichloroethylene	7.5	0.075
cis-Dichloroethylene	4.3	0.043
Carbon tetrachloride	2.6	0.026
Trichloroethylene	5.6	0.056
Perchloroethylene	9.9	0.099
Total VOC	40.5	0.40
Air	59.5	0.60
Total	100.0	1.0

[a] See ref 14.

[b] g of emission per kg of perchloroethylene produced.

does not include storage, handling, fugitive, or secondary emissions. The composition and flow of the uncontrolled emissions in the gas from the reactor vent (A), in the gas from the drying column vent (B), and in the gas from the distillation vents (C) are given in Tables IV-10—12 respectively.[4,16,17]

D. VINYLIDENE CHLORIDE

The process flow diagram (Fig. III-5) for the production of vinylidene chloride from 1,1,2-trichloroethane represents the processes used by Dow Chemical Company[5,18] and PPG Industries, currently the only domestic producers of vinylidene chloride.[2,3] Emissions from the reactor vent (A) are composed of vinylidene chloride, monochloroacetylene, and nitrogen and result from the purging of the reactor to prevent the accumulation of monochloroacetylene in the liquid vinylidene chloride product. An estimate of the reactor vent gas composition is given in Table IV-13.

An estimate of the composition of the distillation column vent (B), the other source of process emissions, is given in Table IV-14. The estimated quantities of emissions from both sources (vents A and B) are based on information from two plants[6,18] and the total is given in Table IV-7.

Table IV-10. Estimated Composition of Reactor Vent Gas from an Oxychlorination Plant for Perchloroethylene and Trichloroethylene[a]

Component	Composition (wt %)	Emission Ratio[b] (g/kg)
Chlorinated C_2's (VOC)	22.5	21.3
Hydrogen chloride	0.5	0.5
Carbon dioxide	69.5	65.5
Nitrogen	7.5	7.1
Total	100	94.4

[a] See ref 4.

[b] g of emission per kg of perchloroethylene and trichloroethylene produced.

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Table IV-11. Estimated Composition of Drying Column Vent Gas from an Oxychlorination Plant for Perchloroethylene and Trichloroethylene[a]

Component	Composition (wt %)	Emission Ratio (g/kg)[b]
trans-Dichloroethylene	26.0	0.65
Vinyl chloride	21.0	0.52
Vinylidene chloride	16.0	0.40
Perchloroethylene/trichloroethylene	0.3	0.0075
Other chlorinated C_2's	24.7	0.62
Total VOC	88.0	2.2
Nitrogen	12.0	0.30
Total	100	2.5

[a] See ref 4.

[b] g of emission per kg of perchloroethylene and trichloroethylene produced.

Table IV-12. Estimated Composition of Distillation Vent Gas from an Oxychlorination Plant for Perchloroethylene and Trichloroethylene[a]

Component	Composition (wt %)	Emission Ratio (g/kg)[b]
trans-Dichloroethylene	39	0.225
cis-Dichloroethylene	11	0.063
Vinylidene chloride	17	0.098
Perchloroethylene	13	0.075
Trichloroethylene	13	0.075
Other chlorinated C_2's	2	0.012
Total VOC	95	0.55
Nitrogen	5	0.029
Total	100	0.58

[a] See ref 4.

[b] g of emission per kg of perchloroethylene and trichloroethylene produced.

Table IV-13. Estimated Composition of Vent Gas from Reactor Section of a Vinylidene Chloride Plant[a]

Component	Composition (wt %)	Emission Ratio (g/kg)[b]
Vinylidene chloride	56	6.2
Monochloroacetylene	8	0.9
Nitrogen	36	4.0

[a] See refs 3, 4, and 5.

[b] g of emissions per kg of product produced.

Table IV-14. Estimated Composition of Distillation Vent Gas from a Vinylidene Chloride Plant[a]

Component	Composition (wt %)	Emission Ratio (g/kg)[b]
Vinylidene chloride	50	0.7
Nitrogen	50	0.7

[a] See ref 18.

[b] g of emissions per kg of product produced.

E. REFERENCES*

1. "1,1,1-Trichloroethane," p 9 in Chemical Marketing Reporter (Jan. 17, 1977).

2. S. A. Cogswell, "Ethylene Dichloride," p. 651-5032M in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (February 1979).

3. S. A. Cogswell, "C_2 Chlorinated Solvents," p. 632.3001T in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (December 1978).

4. F. C. Dehn, PPG Industries, letter dated Mar. 14, 1979, to EPA with information on air emissions from the 1,1,1-trichloroethylene, perchloroethylene, and trichloroethylene plants at Lake Charles, LA, in response to EPA request.

5. R. L. Standifer, IT Enviroscience, Inc., Trip Report for Visit to Dow Chemical Co., Freeport, TX, Nov. 9, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

6. B. Dellamea, Dow Chemical, Freeport, TX, Texas Air Control Board Emissions Inventory Questionnaire for 1975.

7. C. C. Masser, "Storage of Petroleum Liquids," pp. 4.3-1—4.3-16 in Compilation of Air Pollutant Emission Factors, 3d ed., Part A, AP-42, EPA, Research Triangle Park, NC (August 1979).

8. D. G. Erikson and V. Kalcevic, IT Enviroscience, Inc., Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

9. F. D. Hobbs and C. W. Stuewe, IT Enviroscience, Inc., Chloromethanes. Methane Chlorination Process (in preparation for EPA, ESED, Research Triangle Park, NC).

10. F. D. Hobbs and C. W. Stuewe, IT Enviroscience, Inc., Carbon Tetrachloride and Perchloroethylene (Hydrocarbon Chlorinolysis Process) (in preparation for EPA, ESED, Research Triangle Park, NC).

11. T. A. Leonard, Vulcan Materials Co., letter dated Mar. 8, 1979, to EPA with information on air emissions from the 1,1,1-trichloroethane plant at Geismar, LA, in response to EPA request.

12. L. M. Elkin, Chlorinated Solvents Report, Report No. 48, A private report by the Process Economics Program, Stanford Research Institute, Menlo Park, CA (February 1969).

13. Z. S. Khan and T. W. Hughes, Monsanto Research Corporation, Source Assessment: Chlorinated Hydrocarbon Manufacture, June 1977 (preliminary draft on file at EPA, ESED, Research Triangle Park, NC).

14. J. B. Worthington, Diamond Shamrock, letter dated Jan. 16, 1979, to EPA with information on air emissions from the perchloroethylene plant at Deer Park, TX, in response to EPA request.

15. W. C. Strader, Ethyl Corp., letter dated Nov. 28, 1978, to EPA with information on air emissions from the perchloroethylene and trichloroethylene plant at Baton Rouge, LA, in response to EPA request.

16. "PPG Industries: Chlorinated Solvents from Ethylene," Chemical Engineering **76**(26), 90,91 (1969).

17. J. F. Knoop and G. R. Neikirk, "Oxychlorinate for Per/Tri," Hydrocarbon Processing **51**(11), 109,110 (1972).

18. J. Beale, Dow Chemical, letter dated Oct. 25, 1978, to EPA with information on air emissions from the vinylidene chloride plant at Plaquemine, LA, in response to EPA request.

*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. APPLICABLE CONTROL SYSTEMS

A. 1,1,1-TRICHLOROETHANE

1. Vinyl Chloride Process

a. Distillation Vent——The stream from the distillation vents (vent A) is the only significant process emission source. The control option selected for the model-plant distillation vent is combustion in an existing incinerator. An estimated VOC reduction of 98% was used to calculate the controlled emissions from this source (see Table V-1), based on the emission factors from AP-42.[1] As the installation of an incinerator solely for the purpose of controlling this source would not be justifiable, this control method is applicable only if an existing combustion chamber can be used. Also, the relatively low concentration of combustible VOC present in this stream (see Table IV-2) would necessitate the use of supplementary fuel to attain the required incineration temperature.

Another option used for the control of the VOC in the distillation vent gases is aqueous scrubbing. An estimated VOC removal efficiency of 90% is attained by one producer using this method.[2] A potential disadvantage of aqueous scrubbing is that a large part of the VOC removed may be emitted as secondary emissions from the effluent water unless the water is subsequently stripped before discharge to the wastewater treatment system.[3] Another disadvantage of aqueous scrubbing is that it is relatively ineffective for the control of the contained vinyl chloride because of the high vapor pressure and low water solubility of vinyl chloride. (Vinyl chloride has been listed as a hazardous pollutant by EPA.)

b. Storing and Handling Emissions——The emissions from the model-plant storage tanks and from the loading of tank cars, tank trucks, and drums are controlled by refrigerated vent condensers.[2] Options for control of storage and handling emissions are covered in another EPA report.[4] Guidelines for storage and handling emission control techniques will be given in a future EPA document.

The controlled storage and handling emissions are given in Table V-1. VOC removal efficiencies were estimated to be 85% for both storage and handling emissions,

Table V-1. Estimates of Controlled VOC Emissions from a Model Plant Producing 1,1,1-Trichloroethane from Vinyl Chloride (136,000 Mg/yr)

Source	Vent Designation (Fig.III-1)	Control Device or Technique	Total VOC Emission Reduction (%)	VOC Emissions	
				Ratio (g/kg)*	Rate (kg/hr)
Distillation vent	A	Combustion in incinerator	98	0.004	0.06
Storage vents					
Intermediate storage	B	Refrigerated vent condenser	85	0.022	0.35
Product storage	C	Refrigerated vent condenser	85	0.061	0.94
Handling—loading tank cars and tank trucks	D	Refrigerated vent condenser	85	0.090	1.4
Fugitive	E	Detection and correction of major leaks	90	0.277	4.3
Secondary					
Wastewater treatment	F	None		0.001	0.02
Incineration of residue or landfill	G,H	None		<0.001	<0.01
Total				0.46	7.1

*g of emission per kg of 1,1,1-trichloroethane produced.

based on a refrigerated vent condenser effluent temperature of -10°C.[2] Higher removal efficiencies can be attained at lower temperatures, with correspondingly higher capital and operating costs and energy requirements.[4]

A refrigerated absorption system is used by one producer to control storage emissions.[5] The efficiency of this system was not reported.

c. Fugitive Emissions——Controls for fugitive emissions from the synthetic organic chemicals manufacturing industry will be discussed in a future EPA document. Emissions from pumps and valves can be controlled by an appropriate leak-detection system and repair and maintenance as needed. Controlled fugitive emissions calculated with the factors given in Appendix C are included in Table V-1; these factors are based on the assumption that major leaks are detected and corrected.

d. Secondary Emissions——Secondary emissions can occur from wastewater treatment and from incineration or landfill of residues.

Wastewater treatment——Estimates of VOC emissions from wastewater treatment indicate they are very small. These estimates are based on the assumption that wastewater streams with significant VOC concentration are steam-stripped to recover the contained organic compounds before the wastewater is discharged to the treatment system.[5] No additional control system has been identified for the model plant. Control of secondary emissions will be discussed in a future EPA report.

Incineration or landfill of residues——Estimates of the VOC emissions resulting from the disposal of liquid and solid residues either by incineration or by landfill indicate they are very small. No control system has been identified for the model plant.

2. Ethane Process

The controlled emission rates and ratios, the control devices or techniques selected, and the estimates of the emission reductions attained for the ethane-based 1,1,1-trichloroethane model plant are given in Table V-2. The comments on specific emission sources and controls for the vinyl chloride—based model plant, presented in Sect. V-A1, also apply to the ethane model.

Table V-2. Estimates of Controlled VOC Emissions from a Model Plant Producing 1,1,1-Trichloroethane from Ethane (29,500 Mg/yr)

Source	Vent Designation (Fig.III-1)	Control Device or Technique	Total VOC Emission Reduction (%)	VOC Emissions Ratio (g/kg)*	VOC Emissions Rate (kg/hr)
Distillation vent	A	Combustion in incinerator	98	0.004	0.014
Storage vents					
Intermediate storage	B	Refrigerated vent condenser	85	0.023	0.08
Product storage	C	Refrigerated vent condenser	85	0.060	0.21
Handling—loading tank cars and tank trucks	D	Refrigerated vent condenser	85	0.090	0.30
Fugitive	E	Detection and correction of major leaks	90	1.28	4.3
Secondary					
Wastewater treatment	F	None		0.001	0.004
Incineration of residue or landfill	G,H	None		<0.003	<0.01
Total				1.5	4.9

*g of emission per kg of 1,1,1-trichloroethane produced.

B. PERCHLOROETHYLENE AND TRICHLOROETHYLENE

1. Chlorination

Refrigerated vent condensers were selected as the control devices for the neutralization and drying area and the distillation vents (A and B, Fig. III-3), and their VOC removal efficiency was estimated to be 80% (see Table V-3), based on limited data from producers of perchloroethylene and trichloroethylene.[2,6,7]

2. Oxychlorination[5]

The estimate of controlled VOC emissions from the oxychlorination process given in Table V-3 is based on the use of thermal oxidizers to control the emissions from the hydrogen chloride absorber vent (A) and the drying column vent (B), with water scrubbers used to control the emissions from the distillation columns vents (C) and product neutralizer vents (D). The combined VOC emissions reduction is about 98% and is based on data reported by PPG. The installation of a thermal oxidizer to control only the emissions from a perchloroethylene/ trichloroethylene process may not be so cost effective as the multipurpose incineration used by PPG.

C. VINYLIDENE CHLORIDE

The estimate of the total controlled process emissions for plants producing vinylidene chloride (Table V-3) was developed from the estimated efficiencies of devices currenty in use by the industry.[2,8] The devices selected as control options for the separate sources and the corresponding emission ratios and efficiencies are given in Table V-4.

Table V-3. Estimates of Controlled Process VOC Emissions from Processes Producing Perchloroethylene, Trichloroethylene, and Vinylidene Chloride

Process	Product	Capacity (Mg/yr)	Control Device	VOC Emission Reduction (%)	VOC Emissions[a] Ratio[b] (g/kg)	VOC Emissions[a] Rate (kg/hr)
Chlorination	Perchloroethylene and/or trichloroethylene	70,000	Refrigerated condensers	80	1.6	13
Oxychlorination	Perchloroethylene and trichloroethylene	180,000	Thermal oxidizers and water scrubbers	98	0.55	10
Dehydrochlorination	Vinylidene chloride	90,000	Thermal oxidizer and water scrubber	97	0.2	2

[a] Storage handling, fugitive, and secondary emissions are not included in these data.

[b] g of emission per kg of product produced.

Table V-4. Estimates of Controlled VOC Emissions from a Vinylidene Chloride Process[a]

Source	Uncontrolled VOC Emission Ratio (g/kg)[b]	Control Device	VOC Emission Reduction (%)	Controlled VOC Emission Ratio (g/kg)[b]
Reactor vent	7.1	Incineration	98	0.14
Distillation vent	0.7	Aqueous scrubber	90	0.07
Total	7.8			0.21

[a] See refs 2 and 8.

[b] g of emissions per kg of vinylidene chloride produced.

D. REFERENCES*

1. T. Lahre, "Natural Gas Combustion," pp. 1.4.-1—1.4-3 in Compilation of Air Pollutant Emission Factors, 3d ed., Part A, AP-42, EPA, Research Triangle Park, NC (August 1977).

2. R. L. Standifer, IT Enviroscience, Inc., Trip Report for Visit to Dow Chemical, Freeport, TX, Nov. 9, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

3. L. J. Thibodeaux, "Air Stripping of Organics from Wastewater. A Compendium," pp. 358—H378 in the Proceedings of the Second National Conference on Complete Watereuse. Water's Interface with Energy, Air, and Solids, Chicago, IL, May 4—8, 1975, sponsored by AIChE and EPA Technology Transfer.

4. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, NC).

5. F. C. Dehn, PPG Industries, letter dated Mar. 14, 1979, to EPA with information on air emissions from the 1,1,1-trichloroethane plant at Lake Charles, LA, in response to EPA request.

6. J. B. Worthington, Diamond Shamrock, letter dated Jan. 16, 1979, to EPA with information on air emissions from the perchloroethylene plant at Deer Park, TX, in response to EPA request.

7. W. C. Strader, Ethyl Corporation, letter dated Nov. 28, 1978, to EPA with information on air emissions from the perchloroethylene and trichloroethylene plant at Baton Rouge, LA, in response to EPA request.

8. J. Beale, Dow Chemical, letter dated Oct. 25, 1978, to EPA with information on air emissions from the vinylidene chloride plant at Plaquemine, LA, in response to EPA request.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VI. IMPACT ANALYSIS

A. 1,1,1-TRICHLOROETHANE

1. Environmental and Energy Impacts

a. Vinyl Chloride Process——Table VI-1 shows the environmental impact of reducing the total VOC emissions by application of the described control systems (Sect. V) to the model plant described in Sects. III and IV. Use of these control devices or techniques results in the reduction of total VOC emissions by 87%, or about 250 Mg/yr for the model plant, resulting in controlled emissions from the model plant of about 37 Mg/yr.

Distillation vent——The incineration of the gas vented from the distillation columns reduces the model-plant total VOC emissions by 26 Mg/yr and consequently reduces the emission of contained vinyl chloride from this source by 1 Mg/yr to about 0.02 Mg/yr (vinyl chloride is listed as a hazardous pollutant by EPA). Because of the low concentration of organics in this stream (2.6 wt %) a net usage of supplementary fuel is required; however, if the recovery of energy from the combustion products is employed,[1,2] the energy impact will be negligible.

The combustion of chlorinated organic compounds results in the presence of hydrogen chloride in the flue gas, and control of the resulting hydrogen chloride emissions may be necessary.

The use of an existing incinerator has the disadvantage of possibly being unavailable when other process units are down.

Other emissions (storage, handling, and fugitive)——Storage and handling emissions are controlled in the model plant by refrigerated vent condensers, and fugitive emissions are controlled by the repair of leaking components. Application of these controls results in a VOC emission reduction of 223 Mg/yr for the model plant. Energy requirements for the control of storage and handling emissions are covered in a separate EPA report.[3]

Table VI-1. Environmental Impact of Controlled Model Plant Producing 1,1,1-Trichloroethane from Vinyl Chloride

			VOC Emission Reduction	
Emission Source	Vent Designation (Fig.III-1)	Control Device or Technique	(%)	(Mg/yr)
Distillation vent	A	Combustion in incinerator	98	26
Storage vents				
Intermediate storage	B	Refrigerated vent condensers	85	29
Product storage	C	Refrigerated vent condensers	85	78
Handling—loading tank cars and tank trucks	D	Refrigerated vent condensers	85	71
Fugitive	E	Detection and correction of major leaks	90	45
Secondary				
Wastewater treatment	F	None		
Incineration of residue or landfill	G,H	None		——
Total				249

b. Ethane Process—Table VI-2 shows the environmental impact of reducing the total VOC emissions by application of the described control systems (Sect. V) to the model plant described in Sects. III and IV. Use of these control devices or techniques results in the reduction of total VOC emissions by 88%, or about 90 Mg/yr for the model plant, resulting in controlled emissions from the model plant of about 12 Mg/yr.

Distillation vent—The incineration of the gas vented from the distillation columns reduces the model-plant VOC emissions by 6 Mg/yr. The concentration of VOC in this stream is high (approximately 50%), and auxiliary fuel is not required for combustion. The hydrogen chloride formed from the combustion of the contained chlorinated organic compounds may require control of hydrogen chloride in the flue gas.

Other emissions (storage, handling, and fugitive)—Storage and handling emissions are controlled in the model plant by refrigerated vent condensers, and fugitive emissions are controlled by the repair of leaking components. Application of these controls results in a VOC emission reduction of 84 Mg/yr for the model plant. Energy requirements for the control of storage and handling emissions are covered in a separate EPA report.[3]

c. 1979 Industry Emissions—The total VOC emissions from the domestic 1,1,1-trichloroethane industry are estimated at 236 Mg and include estimated emissions from the process, fugitive, secondary, and storage and handling sources. This estimate is based on a projected 1979 level of production of 323,000 Mg. The estimated emissions were determined by applying the emission ratios from Tables IV-1, IV-4, V-1, and V-2. Process emissions are estimated to be 90% controlled, storage and handling emissions to be 94% controlled, and fugitive emissions to be uncontrolled. Emissions from secondary sources are believed to be negligible.

2. Cost Control Impact

The cost control impact described below relates to both the vinyl chloride process and the ethane process.

Table VI-2. Environmental Impact of Controlled Model Plant Producing 1,1,1-Trichloroethane from Ethane

Emission Source	Vent Designation (Fig.III-2)	Control Device or Technique	VOC Emission Reduction	
			(%)	(Mg/yr)
Distillation vent	A	Combustion in incinerator	98	6
Storage vents				
Intermediate storage	B	Refrigerated vent condensers	85	6
Product storage	C	Refrigerated vent condenser	85	17
Handling—loading tank cars and tank trucks	D	Refrigerated vent condensers	85	16
Fugitive	E	Detection and correction of major leaks	90	45
Secondary				
Wastewater treatment	F	None		
Incineration of residue or landfill	G,H	None		—
Total				90

a. Process Vents—Emissions of VOC from the distillation vent are relatively small and incineration is feasible only if an existing incinerator can be used; however, the plants that currently produce 1,1,1-trichloroethane also usually produce other chlorinated organic compounds[4,5] and may dispose of vent gases and chlorinated residues by incineration.[6] The predominant cost of using an existing incinerator would be installation of the piping necessary to transfer the distillation vent gas from the 1,1,1-trichloroethane unit to the incinerator. As the cost of the required piping will depend primarily on the distance of the 1,1,1-trichloroethane plant from the incinerator, which can vary greatly, the cost impact was not determined.

b. Storage and Handling Sources—The control system for storage and handling sources is the use of refrigerated vent condensers. Another EPA report covers storage and handling emissions and their applicable controls for all the synthetic organic chemicals manufacturing industry.[3]

c. Fugitive Sources—A future EPA document will cover fugitive emissions and their applicable controls for all the synthetic organic chemicals industry.

d. Secondary Sources—No control system has been identified for controlling the secondary emissions from wastewater treatment or from the disposal of residues by incineration or landfill. A future EPA document will cover secondary emissions and their applications for all the synthetic organic chemicals manufacturing industry.

B. PERCHLOROETHYLENE AND TRICHLOROETHYLENE

1. Environmental Impact

Table VI-3 lists the estimated current VOC emissions from the chlorination process and from the oxychlorination process for producing perchloroethylene and trichloroethylene. These estimates are based on projected production rates for 1979 of 301,000 Mg of perchloroethylene, of which 108,000 Mg is estimated to be produced by chlorination or oxychlorination, and 132,000 Mg of trichloroethylene. These projections were calculated from reported 1977 production and estimated annual growth rates[4,7] and the production rate of each producer was then calculated as

Table VI-3. Estimate of Current Industry Emissions from Processes Producing Perchloroethylene, Trichloroethylene, and Vinylidene Chloride

Process	Product	Control Device	1979 VOC Emissions (Mg)*
Chlorination	Perchloroethylene and/or trichloroethylene	Refrigerated condensers	250
Oxychlorination	Perchloroethylene and trichloroethylene	Thermal oxidizers and water scrubbers	70
Dehydrochlorination	Vinylidene chloride	Thermal oxidizers and water scrubbers	20

*Storage handling, fugitive, and secondary emissions are not included in these data.

if all were operating at the same per cent of capacity. The reported emission ratios by each producer[8—11] were then applied to projections of production to obtain the estimated 1979 VOC emissions.

2. Other Impacts

Energy and control cost impacts have not been determined for the control devices selected in Sect. V.

C. VINYLIDENE CHLORIDE

1. Environmental Impact

The estimated current VOC emissions from the production of vinylidene chloride are given in Table VI-3. These estimates are based on a projected production rate for 1979 of 86,000 Mg, determined by adjusting the reported 1978 production rate by the estimated annual growth rate.[5] The reported[9—11] emission ratios by producer were then applied to the projections of production to obtain the estimated 1979 VOC emissions.

These estimates include emissions from the processes only, not those from storage and handling, secondary, or fugitive sources. Emissions from these sources are believed to be typical for the synthetic organic chemicals manufacturing industry.

2. Other Impacts

Energy and control cost impacts have not been determined for the control devices selected in Sect. V.

D. REFERENCES*

1. Y. H. Kiang, "Controlling Vinyl Chloride Emissions," Chemical Engineering Progress 72(12), 37—41 (1976).

2. C. G. Bertram, "Minimizing Emissions from Vinyl Chloride Plants," Environmental Science and Technology 11(9), 864—868 (1977).

3. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, NC).

4. S. A. Cogswell, "C_2 Chlorinated Solvents," pp. 632.3000A—F and 632.3001A—632.3002A in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (December 1978).

5. S. A. Cogswell, "Ethylene Dichloride," pp. 651.5031A—F and 651.5032A—561.5033I in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (Febaruary 1979).

6. F. D. Hobbs and J. A. Key, IT Enviroscience, Inc., Ethylene Dichloride (in preparation for EPA, ESED, Research Triangle Park, NC).

7. "(632.3001J) C_2 Chlorinated Solvents," p. 233 in Chemical Economics Handbook, Manual of Current Indicators—Supplemental Data, Chemical Information Services, Stanford Research Institute, Menlo Park, CA (April 1979).

8. J. B. Worthington, Diamond Shamrock, letter dated Jan. 16, 1979, to EPA with information on air emissions from the perchloroethylene plant at Deer Park, TX, in response to EPA request.

9. R. L. Standifer, IT Enviroscience, Inc., Trip Report for Visit to Dow Chemical USA, Freeport, TX, Nov. 9, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

10. W. C. Strader, Ethyl Corp., letter dated Nov. 28, 1978, to EPA with information on air emissions from the perchloroethylene and trichloroethylene plant at Baton Rouge, LA, in response to EPA request.

11. F. C. Dehn, PPG Industries, Inc., letter dated Mar. 14, 1979, to EPA in response to request for information on the air emissions from the 1,1,1-trichloroethane, perchloroethylene, and trichloroethylene processes at Lake Charles, LA.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VII. SUMMARY

A. 1,1,1-TRICHLOROETHANE

1,1,1-Trichloroethane is currently produced by the chlorination of 1,1-dichloroethane, produced from vinyl chloride and the chlorination of ethane. The domestic producton capacity of 1,1,1-trichloroethane by the end of 1979 is expected to be about 590,000 Mg,[1] not including the capacity of a plant that produced 1,1,1-trichloroethane from vinylidene chloride, which was shut down in 1978.[2] At an estimated annual growth rate in 1,1,1-trichloroethane consumption of 6%, the industry is expected to operate at less than capacity through 1981.

Emission sources and uncontrolled and controlled emission rates for the two model plants are given in Tables VII-1 and VII-2. The only significant process emission sources of both processes are the distillation vents, which are controlled in the models by combustion in existing incinerators.

The model-plant 1,1,1-trichloroethane storage and handling emissions are controlled by refrigerated vent condensers. Potential secondary emissions are minor. The total 1,1,1-trichloroethane industry VOC emissions are estimated at 218 Mg in 1979, with most of the uncontrolled VOC emissions coming from fugitive, storage, and handling emissions.

Table VII-1. Emission Summary for 1,1,1-Trichloroethane Model Plant, Vinyl Chloride Process (136,000 Mg/yr)

Emission	Vent Designation (Fig.III-1)	VOC Emission Rate (kg/hr) Uncontrolled	VOC Emission Rate (kg/hr) Controlled
Distillation vent	A	3.0	0.06
Storage vents			
Intermediate storage	B	2.3	0.35
Product storage	C	6.2	0.94
Handling—loading of tank cars, tank trucks, and drums	D	9.5	1.4
Fugitive	E	19.5	4.3
Secondary			
Wastewater treatment	F	0.02	0.02
Incineration of residue or landfill	G,H	<0.01	<0.01
Total		40.5	7.1

Table VII-2. Emission Summary for 1,1,1-Trichloroethane Model Plant, Ethane Process (29,500 Mg/yr)

Emission	Vent Designation (Fig.III-2)	VOC Emission Rate (kg/hr)	
		Uncontrolled	Controlled
Distillation vent	A	0.7	0.014
Storage vents			
Intermediate storage	B	0.5	0.08
Product storage	C	1.4	0.21
Handling—loading of tank cars, tank trucks, and drums	D	2.1	0.30
Fugitive	E	19.5	4.3
Secondary			
Wastewater treatment	F	0.004	0.004
Incineration of residue or landfill	G,H	<0.01	<0.01
Total		24.2	4.9

B. REFERENCES*

1. S. A. Cogswell, "Ethylene Dichloride," pp. 651.5031A—F and 651.5032A—651.5033I in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (February 1979).

2. S. A. Cogswell, "C_2 Chlorinated Solvents," pp. 632.3000A—F and 632.3001A—632.3002A in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (December 1978).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

APPENDIX A
PHYSICAL PROTERTIES OF 1,1,1-TRICHLOROETHANE, PERCHLOROETHYLENE, TRICHLOROETHYLENE, AND VINYLIDENE CHLORIDE

Table A-1. Properties of 1,1,1-Trichloroethane*

Synonyms	Methyl chloroform, α-trichloroethan
Molecular formula	$C_2H_3Cl_3$
Molecular weight	133.41
Physical state	Liquid
Vapor pressure	130.86 mm Hg at 24°C
Vapor specific gravity	4.55
Boiling point	74.1°C
Melting point	-30.41°C
Density	1.3390 g/ml at 20°C/4°C
Water solubility	Insoluble

*From: J. Dorigan _et al_., "1,1,1-Trichloroethane," p. AIV-238 in _Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Organic Chemicals (Chemicals O-Z)_, MTR-7248, Rev. 1, Appendix IV, Mitre Corp., McLean, VA (September 1976).

Table A-2. Properties of Perchloroethylene*

Synonyms	Tetrachloroethylene, carbondichloride (sic*), ethylene tetrachloride, tetrachloroethene
Molecular formula	C_2Cl_4
Molecular weight	165.82
Physical state	Liquid
Vapor pressure	18.47 mm Hg at 25°C
Vapor specific gravity	5.83
Boiling point	121.20°C
Melting point	-19°C
Density	1.6227 g/ml at 20°C/4°C
Water solubility	Insoluble

*From: J. Dorigan et al., "Perchloroethylene," p. AIV-24 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Organic Chemicals (Chemicals O-Z), MTR-7248, Rev. 1, Appendix IV, Mitre Corp., McLean, VA (September 1976).

Table A-3. Properties of Trichloroethylene*

Synonyms	Ethylene trichloride, ethinyl trichloride, trichloroethene, acetylene trichloride
Molecular formula	C_2HCl_3
Molecular weight	131.39
Physical state	Liquid
Vapor pressure	77.5 mm Hg at 25°C
Vapor specific gravity	4.53
Boiling point	87°C
Melting point	-73°C
Density	1.4642 g/ml at 20°C/4°C
Water solubility	Slightly

*From: J. Dorigan *et al*., "Trichloroethylene," p. AIV-242 in *Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Organic Chemicals (Chemicals O-Z)*, MTR-7248, Rev. 1, Appendix IV, Mitre Corp., McLean, VA (September 1976).

Table A-4. Properties of Vinylidene Chloride*

Synonyms	1,1-Dichloroethylene
Molecular formula	$C_2H_2Cl_2$
Molecular weight	97.0
Physical state	Volatile liquid
Vapor pressure	617.14 mm Hg at 20°C
Boiling point	37°C
Melting point	-122.53°C
Density	1.213 g/ml at 20°C/4°C
Water solubility	Insoluble

*From: J. Dorigan et al., "Vinylidene Chloride," p. AIV-290 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Organic Chemicals (Chemicals O-Z), MTR-7248, Rev. 1, Appendix IV, Mitre Corp., McLean, VA (September 1976).

APPENDIX B

AIR-DISPERSION PARAMETERS

Table B-1. Air-Dispersion Parameters for 1,1,1-Trichloroethane (Vinyl Chloride Feed) Model Plant with a Capacity of 136,000 Mg/yr

Source	VOC Emission Rate (g/sec)	Height (m)	Diameter (m)	Discharge Temperature (K)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
			Uncontrolled Emissions			
Distillation vent	0.83	20	0.1	300	0.026	3.3
Storage vents						
Intermediate (4)	0.12 (each)	7.3	5.7	300		
Intermediate (2)	0.07 (each)	7.3	4.1	300		
Product (4)	0.43 (each)	9.8	8.8	300		
Handling—loading tank cars and tank trucks	2.63	4	0.5	300		
Fugitive*	5.41					
Secondary—wastewater treatment	0.0055	1	30	300		
			Controlled Emissions			
Incinerator (distillation vent)	0.016	20		750		
Refrigerated vent condenser (intermediate storage)	0.09	20	0.1	263	0.0016	0.21
Refrigerated vent condenser (product storage and handling)	0.65	20	0.1	263	0.012	1.50
Fugitive*	1.19					

*Distributed over an area of 150 m X 400 m.

Table B-2. Atmospheric Dispersion Parameters for 1,1,1-Trichloroethane (Ethane Feed) Model Plant with a Capacity of 29,500 Mg/yr

Source	VOC Emission Rate (g/sec)	Height (m)	Diameter (m)	Discharge Temperature (K)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
Uncontrolled Emissions						
Distillation vent	0.19	20	0.1	300	0.000018	0.023
Storage vents						
Intermediate (4)	0.029	4.9	3.8	300		
Intermediate (2)	0.016	2.4	3.9	300		
Product (4)	0.10	7.3	5.5	300		
Handling—loading tank cars and tank trucks	0.57	4	0.5	300		
Fugitive*	5.41					
Secondary—wastewater treatment	0.001	1	30	300		
Controlled Emissions						
Incinerator (distillation vent)	0.004	20		750		
Refrigerated vent condenser (intermediate storage)	0.03	20	0.1	263	0.0005	0.067
Refrigerated vent condenser (product storage and handling)	0.14	20	0.1	263	0.0025	0.32
Fugitive*	1.19					

*Distributed over an area of 150 m X 400 m.

APPENDIX C

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX D

EXISTING PLANT CONSIDERATIONS

A. GENERAL

Table D-1[1]—[3] summarizes the control devices currently used by producers of 1,1,1-trichloroethane, perchloroethylene, trichloroethylene, and vinylidene chloride. Information for this report was obtained from a site visit to a manufacturer of these products (a trip report[1] is on file at ESED in Durham, NC) and from responses to requests for information from other manufacturers. Pertinent information concerning emissions and the corresponding control devices used by existing plants is given here.

B. 1,1,1-TRICHLOROETHANE

The only significant process emission sources reported by 1,1,1-trichloroethane manufacturers are the distillation column vents. Emissions are controlled by scrubbing with water at the Dow Freeport, TX, plant,[1] with an estimated VOC removal efficiency of approximately 90% attained. At the PPG Lake Charles, LA, plant distillation vent emissions are compressed and recycled to the EDC process, where the contained VOC is either consumed or is combined with the emissions from the EDC process and eventually incinerated,[2] with an estimated VOC removal efficiency of greater than 98%. Vulcan at Geismer, LA, reports the use of glycol pots for controlling this emission source.[3] No information was obtained as to the function or efficiency of these devices.

Refrigerated condensers and refrigerated absorption systems were the predominant devices reported for controlling storage and handling emissions from 1,1,1-trichloroethane manufacture, as well as from perchloroethylene, trichloroethylene, and vinylidene chloride production. The VOC removal efficiencies of these devices were estimated to range from 85 to 90%.

C. PERCHLOROETHYLENE AND TRICHLOROETHYLENE

1. Chlorination Process

Diamond Shamrock uses a chilled-water condenser on its crude drying column and reports a reduction efficiency of about 80%.[4] Ethyl has a refrigerated vent condenser on its atmospheric distillation columns' vents that reduced the VOC by more than 80%. In addition the vent gases from the vent condenser are sent

Table D-1. Emission Control Devices or Techniques Currently Used by Producers of 1,1,1-Trichloroethane, Perchloroethane, Trichloroethylene, and Vinylidene Chloride

		Emission Source		
Product/Process	Producer/Location	Distillation Vents	Other Process Vents	Storage and Handling
1,1,1-Trichloroethane/ vinyl chloride	Dow, Freeport, TX	Water scrubber		Refrigerated vent condensers
	PPG, Lake Charles, LA[b]	Compressed and transferred to EDC process; vents from EDC process incinerated		Refrigerated absorption system
1,1,1-Trichloroethane/ ethane	Vulcan, Geismar, LA[c]	Glycol pot[d]		No record
Perchloroethylene-trichloroethylene/ chlorination	Dow, Freeport, TX	No record	Water scrubbers	Refrigerated condensers; water scrubbers
	Diamond Shamrock, Deer Park, TX	No record	Chilled water[e] condenser	Refrigerated vent condensers
	Ethyl Corp., Baton Rouge, LA	Refrigerated condenser; vented VOC fed to other processes	No record	No record
Perchloroethylene-trichloroethylene/ oxychlorination	PPG, Lake Charles, LA	Water scrubbers	Thermal oxidizer[f]	No record
Vinylidene chloride	Dow, Plaquemine, LA	Currently uncontrolled; to be recycled and ultimately incinerated	Thermal oxidizer[g]	Refrigerated vent condensers
	Dow, Freeport, TX	Water scrubber	Refrigerated condenser[g]	Refrigerated vent condensers

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[a] See ref 1. [b] See ref 2. [c] See ref 3. [d] No information on function or efficiency of this device. [e] Crude drying column vent. [f] HCl absorption system vent and drying system vent. [g] Reactor vent.

to another process.[5] Diamond Shamrock has several refrigerated vent condensers on in-process and product storage tanks and reports removal efficiencies of from 50 to 99%.[4]

Dow reports an efficiency of 85% for refrigerated condensers on its product storage tanks.[6] Dow uses water scrubbers to control the emissions from two process vents although data on the removal efficiency or type of treatment of the wastewater are not available.[1] Water scrubbers on two raw-material tanks are reported to have efficiencies of 90%. Regulators on four in-process pressure tanks have a reported efficiency of 70%.[6]

2. Oxychlorination Process[2]

A thermal oxidizer, one of two that burn liquid and gaseous wastes from the entire chlorinated hydrocarbon comples, is used by PPG to control the emissions from the hydrogen chloride absorption system vent (A, Fig. III-4) and from the drying still vent (B, Fig. III-4). The removal efficiency is greater than 99% and the operating conditions are 1425°C in the combustion chamber with a residence time of 0.4 sec. Water scrubbers are used by PPG to control the emissions from the distillation columns vents (C, Fig. III-4) and the product neutralizers vents (D, Fig. III-4) by removing hydrogen chloride and small amounts of organics.

D. VINYLIDENE CHLORIDE

At the Dow Plaquemine, LA, plant VOC emissions from the reactor vent are controlled by incineration, with an estimated reduction of about 98%.[7] At the Dow Freeport, TX, plant this source is controlled by a refrigerated condenser, with an estimated VOC removal efficiency of 93%.[1] Emissions of VOC from the distillation vent are controlled by an aqueous scrubber at the Dow Freeport, TX, plant, with an estimated reduction in VOC emission of approximately 90%.[1] Emissions of VOC from the distillation vent at the Dow Plaquemine, LA, plant are currently uncontrolled; however, changes that are planned include routing the vent to the steam stripper and recycling the stripped gas to the dehydrochlorination reactor, where the contained noncondensible gases will be included with the current reactor vent stream and routed to the incinerator.[7] This should provide a VOC removal efficiency of about 98% for the distillation vent stream.

Data are not currently available on the control devices and controlled emissions for PPG's Lake Charles, LA, vinylidene chloride plant. Dow and PPG are currently the only domestic producers of vinylidene chloride.

E. RETROFITTING CONTROLS

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of the costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems in existing palnts than to install a control system during construction of a new plant.

F. REFERENCES*

1. R. L. Standifer, IT Enviroscience, Inc., Trip Report for Visit to Dow Chemical USA, Freeport, TX, Nov. 9, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

2. F. C. Dehn, PPG Industries, Inc., letter dated Mar. 14, 1979, to EPA in response to request for information on the air emissions from the 1,1,1-trichloroethane, perchloroethylene, and trichloroethylene processes at Lake Charles, LA.

3. T. A. Leonard, Vulcan Materials Co., letter dated Mar. 8, 1979, to EPA with information on air emissions from the 1,1,1-trichloroethane plant at Geismar, LA, in response to EPA request.

4. J. B. Worthington, Diamond Shamrock, letter dated Jan. 16, 1979, to EPA with information on air emissions from the perchloroethylene plant at Deer Park, TX, in response to EPA request.

5. W. C. Strader, Ethyl Corporation, letter dated Nov. 28, 1978, to EPA with information on air emissions from the perchloroethylene and trichloroethylene plant at Baton Rouge, LA, in response to EPA request.

6. R. S. McKneely, Dow Chemical, Freeport, TX, Texas Air Control Board Emissions Inventory Questionnaire for 1975.

7. J. Beale, Dow Chemical, letter dated Oct. 25, 1978, to EPA with information on air emissions from the cinylidene chloride plant at Plaquemine, LA, in response to EPA request.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

REPORT 5

CHLOROMETHANES BY METHANE CHLORINATION PROCESS

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Research Triangle Park, North Carolina

February 1981

This report contains certain information which has been extracted from the Chemical Economics Handbook, Stanford Research Institute. Wherever used, it has been so noted. The proprietary data rights which reside with Stanford Research Institute must be recognized with any use of this material.

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^{9}	1 Gg = 1 X 10^{9} grams
M	mega	10^{6}	1 Mg = 1 X 10^{6} grams
k	kilo	10^{3}	1 km = 1 X 10^{3} meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Four volatile organic compounds (VOC) -- methyl chloride, methylene chloride, chloroform, and carbon tetrachloride -- comprise the group commonly referred to as "chloromethanes." These compounds were selected for study because preliminary estimates indicated that their production causes relatively high VOC emissions.

There are several processes by which chloromethanes are produced either as co-products or individually: (1) the methanol hydrochlorination and methyl chloride chlorination processes, which are described in a similar report;[1] (2) methane chlorination, which yields all four chloromethanes as co-products and is the process described in this report; (3) hydrocarbon chlorinolysis, which yields carbon tetrachloride and perchloroethylene as co-products and which also is described in a similar report;[2] and (4) carbon disulfide chlorination, which produces carbon tetrachloride.

B. METHYL CHLORIDE

1. General Description

Methyl chloride is a gas at ambient conditions but is handled commercially in liquid form (see Appendix A for pertinent physical properties). It is produced by methanol hydrochlorination or by methane chlorination. Emissions from its manufacture include all the chloromethanes.

2. Usage and Growth

The end uses and expected growth rates of methyl chloride are given in Table II-1. The predominant use of methyl chloride is as an intermediate in the production of silicones and in the production of tetramethyllead, a gasoline additive. The expected increase in usage as an intermediate for silicone production combined with decreases in usage as an intermediate for tetramethyllead production, which is being restricted as a gasoline additive,[3] will result in nearly static production patterns for methyl chloride. Large amounts of the methyl chloride manufactured are not recovered as product but are further chlorinated to produce methylene chloride and chloroform. This usage is not included in the production and end-use statistics.[4]

Table II-1. Methyl Chloride Usage and Growth[a]

End Use[b]	Production (%) 1977	Average Annual Growth (%)
Silicone intermediate	63	10-12
Tetramethyllead intermediate	18	-25
Butyl rubber (catalyst solvent)	8	3.5
Miscellaneous	11	NA[c]

[a] See refs 3 and 4.

[b] Amounts consumed as intermediates in continuous production of other chloromethanes not included.

[c] Not available.

The current domestic methyl chloride production capacity is reported to be about 283,000 Mg/yr,[4] with the 1979 production utilizing only about 72% of that capacity.[5] The annual growth in methyl chloride production is expected to remain static or at best to increase by 5% annually. Even at the 5% annual growth rate, production would reach only about 83% of capacity by 1982. There are no known plans for new methyl chloride production facilities.

3. Domestic Producers

There are ten domestic producers of methyl chloride operating 13 plants. Table II-2 lists the producers, locations, capacities, and processes in use; Fig. II-1 shows the plant locations. The Dow plant at Freeport, TX, produces methyl chloride by chlorination of methane. Allied uses hydrochlorination of methanol for about 95% of its production and uses chlorination of methane for the remaining production.[6] Vulcan operates two chloromethanes facilities at Wichita, KS. One is a recently constructed facility based completely on hydrochlorination of methanol, and the other (older) facility uses both hydrochlorination of methanol and chlorination of methane. Hydrochlorination of methanol accounts for about 90% of the total combined production.[7] All other manufacturers produce methyl chloride by hydrochlorination of methanol. The two Vulcan plants use all the methyl chloride they produce as an intermediate and therefore report no methyl chloride capacity as such. Allied, Diamond Shamrock, Dow, and Stauffer produce the higher chloromethanes in addition to methyl chloride. The ratios of co-products produced at these plants are flexible because the methyl chloride may be separated as product or may be further chlorinated to produce methylene chloride and chloroform. Continental, Dow Corning, Ethyl, General Electric, and Union Carbide produce only methyl chloride.

C. METHYLENE CHLORIDE

1. General Description

Methylene chloride is a heavy, volatile liquid at ambient conditions (see Appendix A for pertinent physical properties) and is produced by chlorination of either methyl chloride or methane. Emissions from its manufacture include all the chloromethanes.

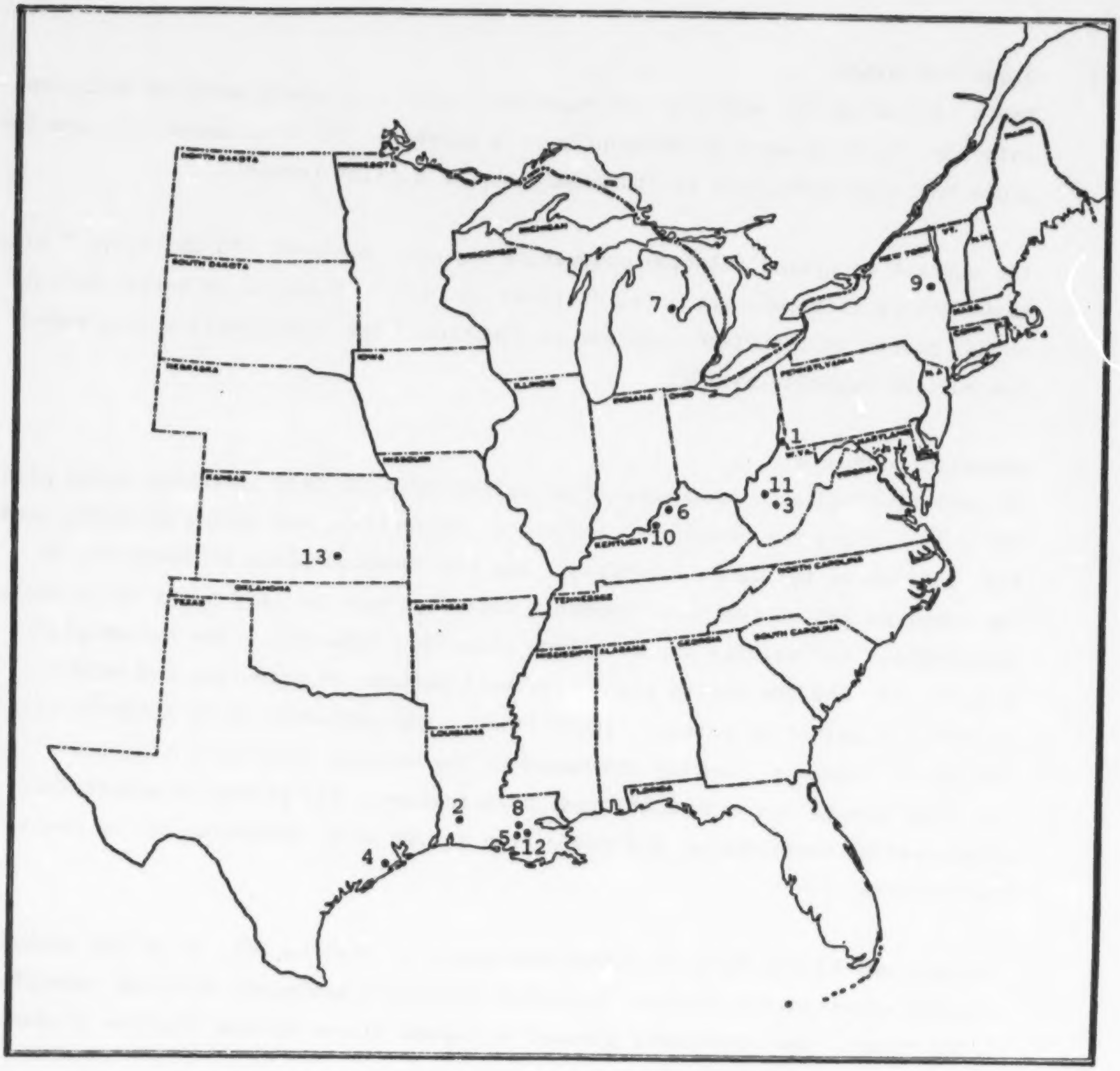
Table II-2. Methyl Chloride Capacity[a]

Plant	1977 Capacity (X 10^3 Mg)	Process
Allied, Moundsville, WV	11[b]	Methanol hydrochlorination and methane chlorination
Continental, Westlake, LA	46	Methanol hydrochlorination
Diamond Shamrock, Belle, WV	11[b]	Methanol hydrochlorination
Dow, Freeport, TX	32[b]	Methane chlorination
Dow, Plaquemine, LA	68[b]	Methanol hydrochlorination
Dow Corning, Carrolton, KY	9	Methanol hydrochlorination
Dow Corning, Midland, MI	7	Methanol hydrochlorination
Ethyl, Baton Rouge, LA	46	Methanol hydrochlorination
General Electric, Waterford, NY	23	Methanol hydrochlorination
Stauffer, Louisville, KY	7[b]	Methanol hydrochlorination
Union Carbide, Institute, WV	23	Methanol hydrochlorination
Vulcan, Geismar, LA	c	Methanol hydrochlorination
Vulcan, Wichita, KS	c	Methanol hydrochorination and methane chlorination
Total	283	

[a] See ref 4.

[b] Production ratios vary with amount of methyl chloride separated as product and amount chlorinated for methylene chloride and chloroform manufacture.

[c] All methyl chloride is chlorinated to methylene chloride and chloroform.



1. Allied, Moundsville, WV
2. Continental, Westlake, LA
3. Diamond Shamrock, Belle, WV
4. Dow, Freeport, TX
5. Dow, Palquemine, LA
6. Dow Corning, Carrolton, KY
7. Dow Corning, Midland, MI
8. Ethyl, Baton Rouge, LA
9. General Electric, Waterford, NY
10. Stauffer, Louisville, KY
11. Union Carbide, Institute, WV
12. Vulcan, Geismar, LA
13. Vulcan, Wichita, KS

Fig. II-1. Locations of Plants Manufacturing Methyl Chloride

2. Usage and Growth

Table II-3 gives the end uses and expected production growth rates of methylene chloride, which is used predominantly as a solvent. Its nonflammability and low acute toxicity contribute to its popularity as a paint remover.

The current methylene chloride production capacity is about 378,000 Mg/yr,[4] with about 75% of that capacity being utilized in 1979.[5] Based on an estimated 11% annual growth in methylene chloride consumption,[3] the demand will nearly equal the current capacity by 1982.

3. Domestic Producers

In 1979 five domestic producers of methylene chloride were operating seven plants. Table II-4 lists the producers, locations, capacities, and processes being used; Fig. II-2 shows the plant locations. The Dow Chemical plant at Freeport, TX, representing 24% of the total domestic capacity, was the only plant using methane chlorination exclusively for methylene chloride production. The Vulcan plant at Wichita, KS, and the Allied plant have both methane chlorination and methyl chloride chlorination process capabilities. Approximately 5% of Allied's capacity and 10% of Vulcan's capacity are based on the methane chlorination process.[6,7] All other plants use methyl chloride chlorination. All producers manufacture chloromethane co-products, and production ratios vary, depending on the desired end products.

Vulcan's new 63,500-Mg/yr chloromethane plant at Wichita, KS, using the methyl chloride chlorination process, provided additional methylene chloride capacity of 36,300 Mg/yr. Dow reportedly planned to expand its methylene chloride production capacity by late 1979.[4]

D. CHLOROFORM

1. General Description

Chloroform is a heavy, volatile liquid at ambient conditions (see Appendix A for pertinent physical properties) and is made by chlorination of methyl chloride or methane. Emissions from chloroform manufacture include all the chloromethanes.

Table II-3. Methylene Chloride Usage and Growth[a,b]

End Use	1977 Production (%)
Paint remover	30
Solvent degreasing	20
Plastics process	9
Exports	18
Aerosol	19
Miscellaneous	4

[a] See ref 4.

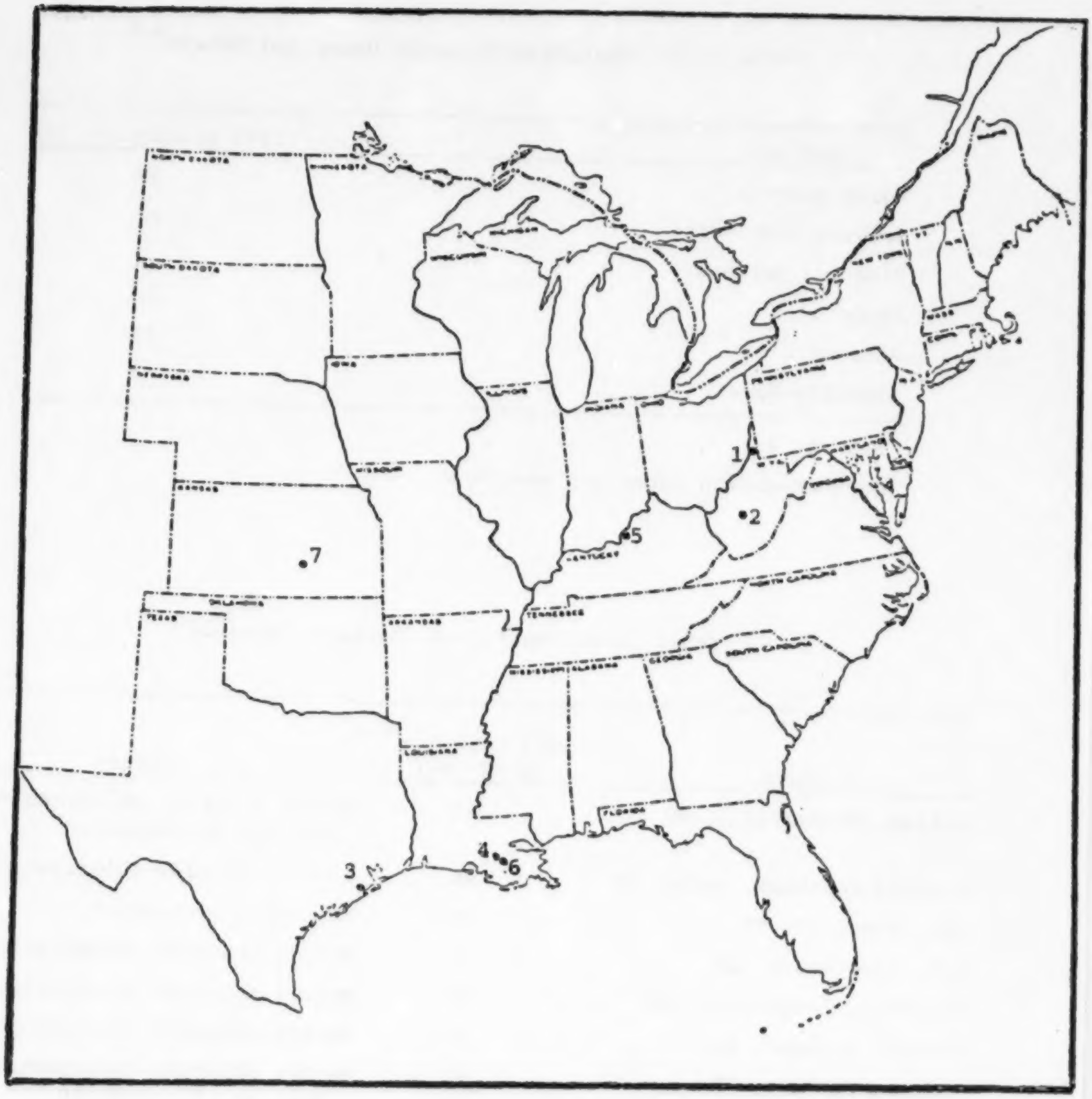
[b] Data on growth rates not available.

Table II-4. Methylene Chloride Capacity[a]

Plant	1977 Capacity[b] (X 10^3 Mg)	Process
Allied, Moundsville, WV	23	Methyl chloride chlorination and methane chlorination
Diamond Shamrock, Belle, WV	50	Methyl chloride chlorination
Dow, Freeport, TX	92	Methane chlorination
Dow, Plaquemine, LA	88	Methyl chloride chlorination
Stauffer, Louisville, KY	28	Methyl chloride chlorination
Vulcan, Geismar, LA	37	Methyl chloride chlorination
Vulcan, Wichita, KS	60	Methyl chloride chlorination and methane chlorination
Total	378	

[a] See ref 4.

[b] Other chloromethanes are manufactured as co-products, and capacities for individual products vary.



1. Allied, Moundsville, WV
2. Diamond Shamrock, Belle, WV
3. Dow, Freeport, TX
4. Dow, Plaquemine, LA
5. Stauffer, Louisville, KY
6. Vulcan, Geismar, LA
7. Vulcan, Wichita, KS

Fig. II-2. Locations of Plants Manufacturing Methylene Chloride

2. Usage and Growth

As is shown in Table II-5, the predominant end use of chloroform is as an intermediate in the manufacture of chlorodifluoromethane. Chlorodifluoromethane can be used as a refrigerant, a solvent, or a propellant or in the manufacture of fluororesins, but its main use is as a refrigerant. A ban on fluorocarbon propellants would not significantly affect its production rate.[4]

The current domestic chloroform production capacity is 237,000 Mg/yr,[4] with 1979 production utilizing about 67% of that capacity.[5] Based on an estimated 8% annual growth in chloroform consumption, production would reach 84% of current capacity by 1982.

3. Domestic Producers

In 1979 five domestic producers were operating seven chloroform-producing plants. Table II-6 lists the producers, locations, capacities, and processes being used; Fig. II-3 shows the plant locations. The Dow Chemical plant at Freeport, TX, is the only facility using methane chlorination exclusively for chloroform production. The capacity of this plant is about 20% of the total domestic capacity. The Allied plant, as well as the Vulcan plant at Wichita, KS, has both methane chlorination and methyl chloride chlorination process capabilities. Approximately 5% of Allied's capacity and 10% of Vulcan's capacity are based on methane chlorination.[6,7] All other plants use methyl chloride chlorination exclusively for chloroform production. All producers manufacture chloromethane co-products, and production ratios vary, depending on the desired end products.

Vulcan's new 63,500-Mg/yr chloromethanes plant at Wichita, KS, which was completed in 1977, provided an additional capacity of 27,200 Mg/yr. Dow scheduled an increase in capacity at Freeport, TX, which was to have been brought on-stream late in 1979.[4]

E. CARBON TETRACHLORIDE

1. General Description

Carbon tetrachloride is a heavy, volatile liquid at ambient conditions (see Appendix A for pertinent physical properties), and is produced by methane chlorination, chlorinolysis of mixed hydrocarbons, or carbon disulfide chlorination. It also is a by-product in the methyl chloride chlorination process.

Table II-5. Chloroform Usage[a,b]

	1974 Production (%)
Chlorodifluoromethane	
Refrigerant, solvent, propellant	91
Exports	7
Miscellaneous	2

[a] See ref 4.

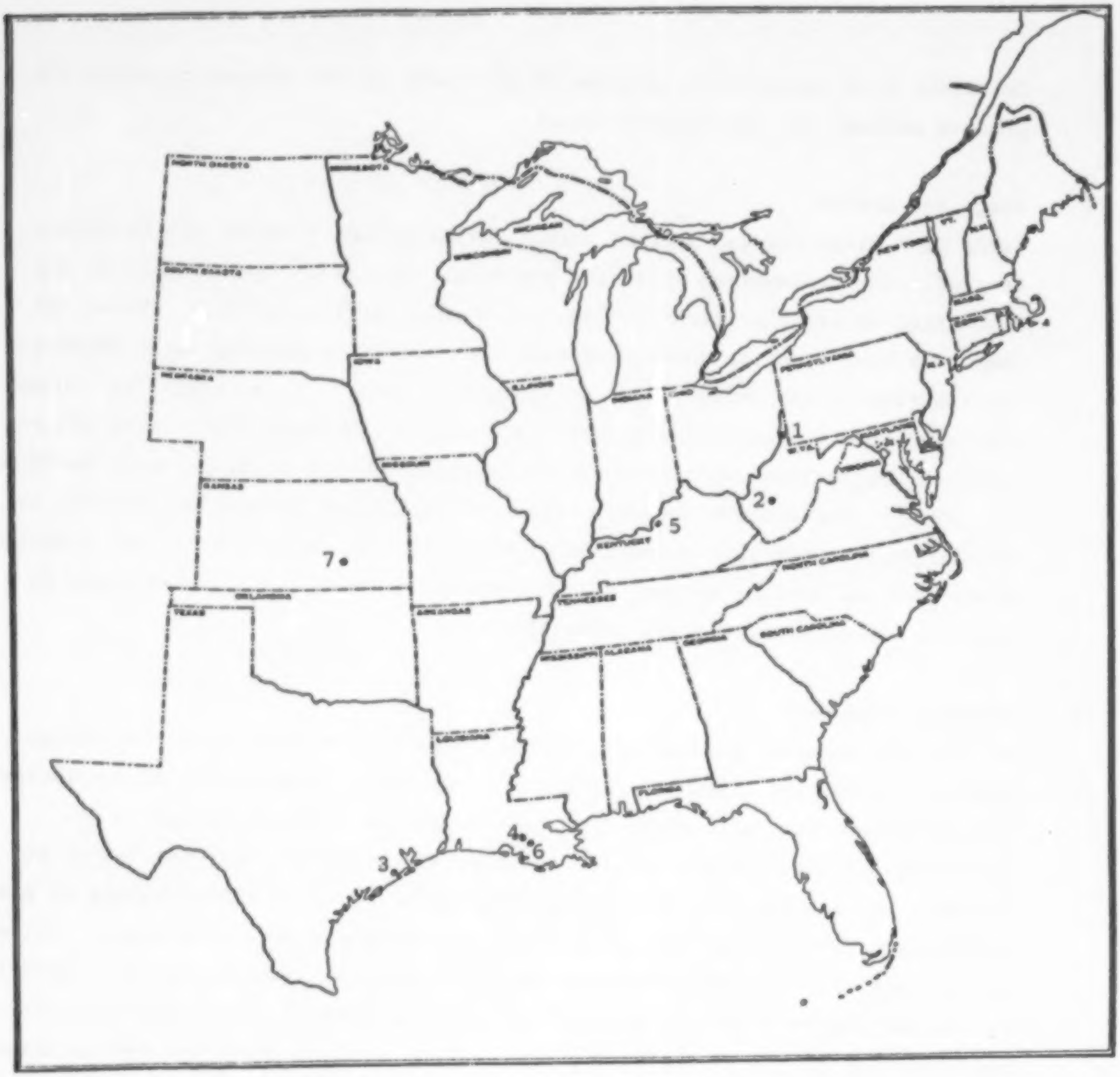
[b] Data on growth rates not available.

Table II-6. Chloroform Capacity[a]

Plant	1979 Capacity[b] (X 10^3 Mg)	Process
Allied, Moundsville, WV	14	Methyl chloride chlorination and methane chlorination
Diamond Shamrock, Belle, WV	18	Methyl chloride chlorination
Dow, Freeport, TX	46	Methane chlorination
Dow, Plaquemine, LA	46	Methyl chloride chlorination
Stauffer, Louisville, KY	34	Methyl chloride chlorination
Vulcan, Geismar, LA	28	Methyl chloride chlorination
Vulcan, Wichita, KS	51	Methyl chloride chlorination and methane chlorination
Total	237	

[a] See ref 4.

[b] Other chloromethanes are manufactured as co-products, and capacities for individual products vary.



1. Allied, Moundsville, WV
2. Diamond Shamrock, Belle, Wv
3. Dow, Freeport, TX
4. Dow, Plaquemine, LA
5. Stauffer, Louisville, KY
6. Vulcan, Geismar, LA
7. Vulcan, Wichita, KS

Fig. II-3. Locations of Plants Manufacturing Chloroform

Emissions from carbon tetrachloride manufactured by the methane chlorination process include all the chloromethanes.

2. Usage and Growth

Table II-7 gives the end uses of carbon tetrachloride.[5] About 90% of carbon tetrachloride consumption in recent years has been as an intermediate in the production of trichlorofluoromethane and dichlorodifluoromethane. These two compounds have been the subject of much controversy concerning their potential contribution to the depletion of stratospheric ozone. As a result the consumption of carbon tetrachloride between 1974 and 1976 dropped 27%.[8] (The EPA promulgated regulations controlling fully halogenated chlorofluoroalkanes on March 17, 1978.[9]) The current domestic carbon tetrachloride production capacity is 555,000 Mg/yr, with 1979 production[10] utilizing only about 57% of that capacity. Production may decline as much as 10% annually. There are no known plans to increase carbon tetrachloride capacity.

3. Domestic Producers

In 1979 six domestic producers of carbon tetrachloride were operating eleven plants. Table II-8 lists the producers, locations, capacities, and manufacturing processes; Fig. II-4 shows the plant locations. Dow at Freeport, TX, Pittsburg, CA, and Plaquemine, LA; Stauffer at Louisville, KY; and Vulcan at Geismar, LA, and Wichita, KS, all operate plants based on chlorinolysis of mixed hydrocarbon feed streams and produce perchloroethylene as a co-product. Allied; Dow at Freeport, TX, and Pittsburg, CA; and Vulcan at Wichita, KS, are reported[8] to operate plants using the methane chlorination process, which produces carbon tetrachloride as one of the co-products. Some of these producers may be using methane feed in the chlorinolysis process. Only a small portion of the Allied and Vulcan capacity is based on methane chlorination.[6,7] Stauffer at LeMoyne, AL, and Niagara Falls, NY, operates carbon tetrachloride production plants that use the carbon disulfide chlorination process. FMC operated a carbon disulfide chlorination process at South Charleston, WV, that was shut down in 1979. No information on capacity or raw material is available on the Inland Chemical Corporation plant at Manati, PR. Capacities for all plants other than those using the carbon disulfide chlorination process are flexible since reaction conditions can be adjusted to vary the yields of carbon tetrachloride and its co-products.

Table II-7. Carbon Tetrachloride Usage[a,b]

End Use	1977 Production (%)
Trichlorofluoromethane	33.8
Dichlorodifluoromethane	55
Miscellaneous	11.2

[a] See ref 5.

[b] Data on growth rates not available.

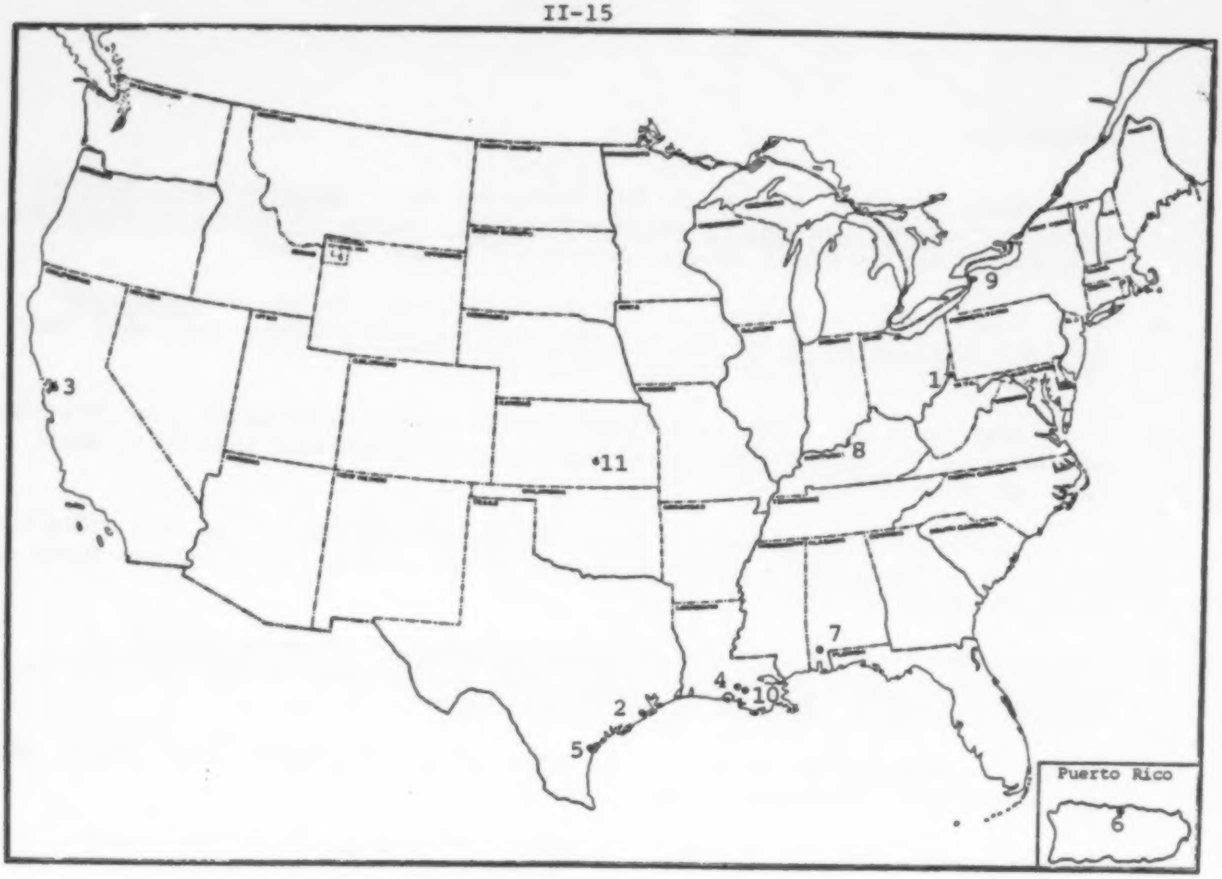
Table II-8. Carbon Tetrachloride Capacity[a]

Plant	1977 Capacity[b] ($X\ 10^3$ Mg)	Process
Allied, Moundsville, WV	4	Methyl chloride chlorination and methane chlorination
Dow, Freeport, TX	61	Methane chlorination and chlorinolysis of mixed hydrocarbon feed with perchloroethylene co-product
Dow, Pittsburg, CA	36	Methane chlorination and chlorinolysis of mixed hydrocarbon feed with perchloroethylene co-product
Dow, Plaquemine, LA	57	Chlorinolysis of mixed hydrocarbon feed with perchloroethylene co-product
Du Pont, Corpus Christi, TX	154	Chlorinolysis of mixed hydrocarbon feed with perchloroethylene co-product
Inland, Manati, PR	c	c
Stauffer, Le Moyne, AL	91	Carbon disulfide chlorination
Stauffer, Louisville, KY	16	Methane chlorination and chlorinolysis of mixed hydrocarbon feed with perchloroethylene co-product
Stauffer, Niagara Falls, NY	68	Carbon disulfide chlorination
Vulcan, Geismar, LA	41	Chlorinolysis of mixed hydrocarbon feed with perchloroethylene co-product
Vulcan, Wichita, KS	27	Methyl chloride chlorination, methane chlorination, and chlorinolysis of mixed hydrocarbon feed with perchloroethylene co-product
Total	555	

[a] See ref 8.

[b] Production ratios are flexible, especially when co-products are involved.

[c] Not available.



(1) Allied Chemical Corp., Moundsville, WV
(2) Dow Chemical Co., Freeport, TX
(3) Dow Chemical Co., Pittsburg, CA
(4) Dow Chemical Co., Plaquemine, LA
(5) Dupont Co., Inc., Corpus Christi, TX
(6) Inland Chemical Corp., Manti, PR
(7) Stauffer Chemical Co., Le Moyne, AL
(8) Stauffer Chemical Co., Louisville, KY
(9) Stauffer Chemical Co., Niagara Falls, NY
(10) Vulcan Materials Co., Geismar, LA
(11) Vulcan Materials Co., Wichita, KS

Fig. II-4. Locations of Plants Manufacturing Carbon Tetrachloride

F. REFERENCES*

1. F. D. Hobbs and C. W. Stuewe, IT Enviroscience, Inc., Chloromethanes Manufactured by Methanol Hydrochlorination and Methyl Chloride Chlorination Processes, (November 1980) (EPA/ESED report, Research Triangle Park, NC).

2. F. D. Hobbs and C. W. Stuewe, IT Enviroscience, Inc., Carbon Tetrachloride and Perchlorethylene by the Hydrocarbon Chlorinolysis Process (September 1980) (EPA/ESED report, Research Triangle Park, NC).

3. A. D. Obshire et al., "CEH Marketing Research Report on Methanol," pp. 674.5023I—674.5033S in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (June 1980).

4. T. F. Killilea, "CEH Product Review on Chlorinated Methanes," pp. 625.2030A—635.2031G in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (April 1979).

5. "Chlorinated Methanes," p. 244 in Chemical Economics Handbook, Manual of Current Indicators--Supplemental Data, Chemical Information Services, Stanford Research Institute, Menlo Park, CA (August 1980).

6. Personal communication between F. D. Hobbs, IT Enviroscience, Inc., and D. Denoon, Allied Chemical, Moundsville, WV, July 25, 1978.

7. Personal communication between F. D. Hobbs, IT Enviroscience, Inc., and T. A. Robinson, Vulcan Materials Co., Wichita, KS, July 28, 1978.

8. E. M. Klapproth, "Carbon Tetrachloride—Salient Statistics," pp 635.2030A—E in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (April 1976).

9. Environmental Protection Agency, "Fully Halogenated Chlorofluoroalkanes," Federal Register, Vol 43, Part II, p 11318 (Mar. 17, 1978).

10. "C_2 Chlorinated Solvents," p 228 in Chemical Economics Handbook, Manual of Current Indicators—Supplemental Data, Chemical Information Services, Stanford Research Institute, Menlo Park, CA (June 1980).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTION

A. INTRODUCTION

Methane can be chlorinated thermally, photochemically, or catalytically, with thermal chlorination being the most important method.[1] Methyl chloride, methylene chloride, chloroform, and carbon tetrachloride are produced in this process by the following reactions:

$$\underset{\text{(methane)}}{CH_4} + \underset{\text{(chlorine)}}{Cl_2} \longrightarrow \underset{\text{(methyl chloride)}}{CH_3Cl} + \underset{\text{(hydrogen chloride)}}{HCl}$$

$$\underset{\text{(methyl chloride)}}{CH_3Cl} + \underset{\text{(chlorine)}}{Cl_2} \longrightarrow \underset{\text{(methylene chloride)}}{CH_2Cl_2} + \underset{\text{(hydrogen chloride)}}{HCl}$$

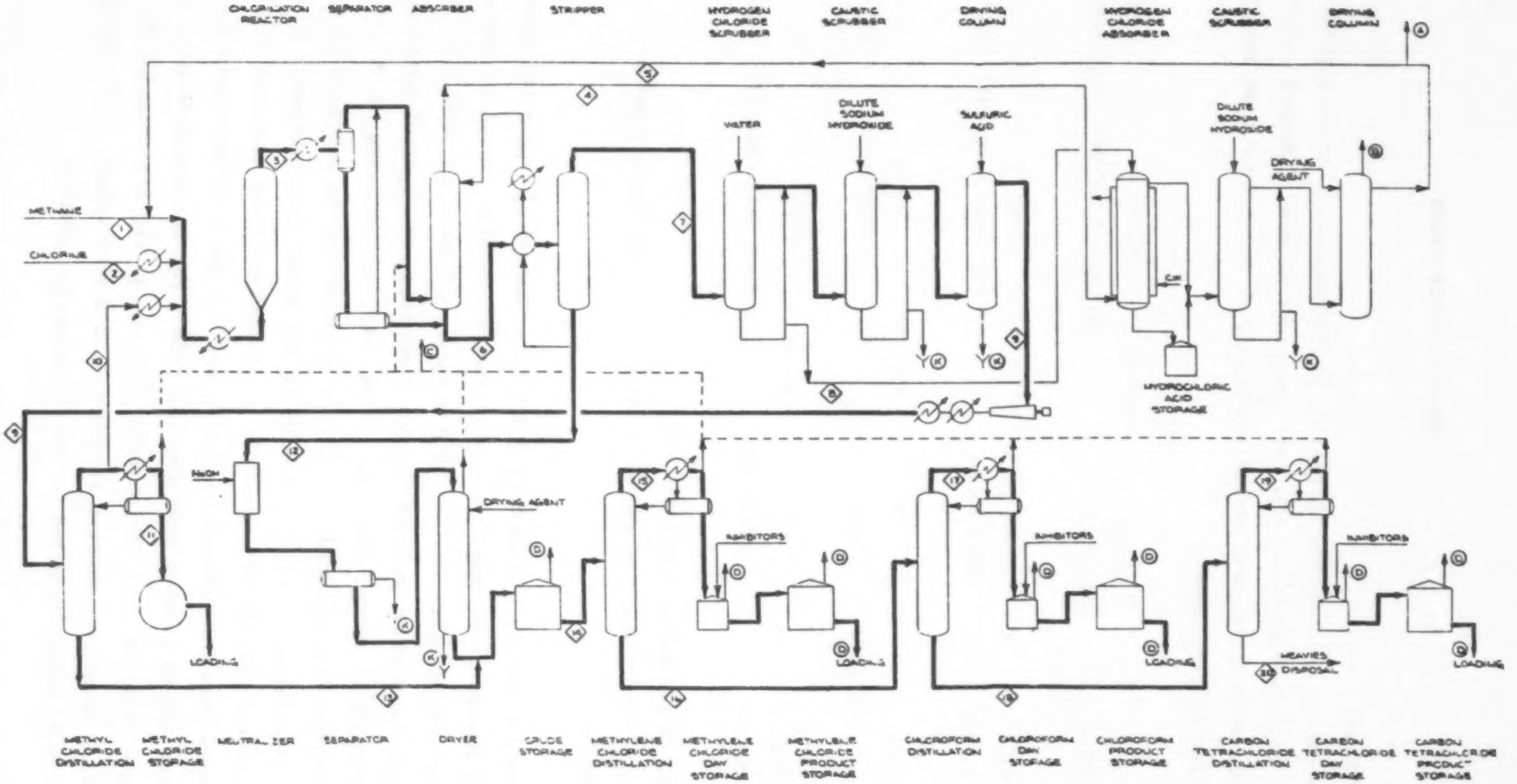
$$\underset{\text{(methylene chloride)}}{CH_2Cl_2} + \underset{\text{(chlorine)}}{Cl_2} \longrightarrow \underset{\text{(chloroform)}}{CHCl_3} + \underset{\text{(hydrogen chloride)}}{HCl}$$

$$\underset{\text{(chloroform)}}{CHCl_3} + \underset{\text{(chlorine)}}{Cl_2} \longrightarrow \underset{\text{(carbon tetrachloride)}}{CCl_4} + \underset{\text{(hydrogen chloride)}}{HCl}$$

B. METHANE CHLORINATION MODEL PROCESS

A typical continuous process flow diagram for the basic process is shown in Fig. III-1.

Methane (Stream 1) is mixed with chlorine (Stream 2); then the mixture is preheated before it is fed to the chlorination reactor, which is operated at a temperature of about 400°C[1] and a pressure of about 200,000 Pa.[2] Nearly 100% chlorine conversion and 65% methane conversion are typical with product yields of about 58.5% methyl chloride, 29.3% methylene chloride, 9.7% chloroform and 2.3% carbon tetrachloride.[3] (Methyl chloride can be recycled to the reactor after separation to enhance yields of the other chloromethanes.) Gases exiting the reactor (Stream 3) are partly condensed and then scrubbed with chilled chloromethanes from the process to absorb most of the chloromethanes from unreacted methane and by-product hydrogen chloride. The unreacted methane and by-product hyrogen chloride from the absorber (Stream 4) are fed serially to a hydrogen chloride absorber, caustic scrubber, and drying column, with the purified methane (Stream 5) being recycled to the chlorination reactor.


CHLORINATION REACTOR
SEPARATOR
ABSORBER
STRIPPER
HYDROGEN CHLORIDE SCRUBBER
CAUSTIC SCRUBBER
DRYING COLUMN
HYDROGEN CHLORIDE ABSORBER
CAUSTIC SCRUBBER
DRYING COLUMN
METHANE
CHLORINE
WATER
DILUTE SODIUM HYDROXIDE
SULFURIC ACID
DILUTE SODIUM HYDROXIDE
DRYING AGENT
CW
HYDROCHLORIC ACID STORAGE
NaOH
DRYING AGENT
INHIBITORS
INHIBITORS
INHIBITORS
LOADING
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HEAVIES DISPOSAL
1
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16
17
18
19
20
A
B
C
D
K
METHYL CHLORIDE DISTILLATION
METHYL CHLORIDE STORAGE
NEUTRALIZER
SEPARATOR
DRYER
CRUDE STORAGE
METHYLENE CHLORIDE DISTILLATION
METHYLENE CHLORIDE DAY STORAGE
METHYLENE CHLORIDE PRODUCT STORAGE
CHLOROFORM DISTILLATION
CHLOROFORM DAY STORAGE
CHLOROFORM PRODUCT STORAGE
CARBON TETRACHLORIDE DISTILLATION
CARBON TETRACHLORIDE DAY STORAGE
CARBON TETRACHLORIDE PRODUCT STORAGE

Fig. III-1. Process Flow Diagram for Manufacture of Chloromethanes by Methane Chlorination Process

Condensed material from the separator and liquid effluent from the absorber are combined (Stream 6) and fed to a stripper. Overheads from the stripper, which include hydrogen chloride, methyl chloride, and some of the higher boiling chloromethanes (Stream 7), are fed to a water scrubber, where most of the hydrogen chloride is removed as weak hydrochloric acid (Stream 8). The overheads are then scrubbed with dilute sodium hydroxide solution to remove residual hydrogen chloride. Water is then removed from the crude chloromethanes in a drying column.

The crude chloromethanes from the drying column (Stream 9) are compressed, condensed, and fed to a methyl chloride distillation column. Methyl chloride from the distillation column can be recycled back to the chlorination reactor (Stream 10) or be condensed and then transferred to storage and loading as product (Stream 11).

Crude methylene chloride, chloroform, and carbon tetrachloride from the stripper (Stream 12) are neutralized, dried, and combined with bottoms from the methyl chloride distillation column (Stream 13) in a crude storage tank. The crude chloromethanes (Stream 14) pass to a methylene chloride distillation column. Methylene chloride from the overheads (Stream 15) is condensed and fed to day storage tanks, where inhibitors may be added for stabilization. Product methylene chloride is transferred to product storage and loading. Bottoms from the methylene chloride distillation column (Stream 16) are fed to a chloroform distillation column, with chloroform overheads (Stream 17) being condensed and fed to day storage tanks, where inhibitors may be added for stabilization. Product chloroform is transferred to storage and loading. Bottoms from the chloroform distillation column (Stream 18) are fed to a carbon tetrachloride distillation column, with carbon tetrachloride overheads (Stream 19) being condensed and fed to day storage tanks, where inhibitors may be added for stabilization. Product carbon tetrachloride is transferred to storage and loading. Bottoms from the carbon tetrachloride distillation column are incinerated.

Vented gases from the four distillation columns could be recycled to the absorber, as is indicated in Fig. III-1.

Process emissions from the model plant result from venting of the inert gases from the recycle methane stream (Vent A, Fig. III-1), from regeneration of the methane recycle stream drying bed (Vent B, Fig. III-1), and from emergency venting of the distillation-area inert gases (Vent C, Fig. III-1).

Fugitive emissions can occur when leaks develop in valves, pump seals, and other equipment. Corrosion could be caused by the hydrogen chloride and chlorine in the process if careful attention is not given to selection of equipment and materials of construction.

Emissions result from the storage of intermediates and products and from the handling of products.

Potential sources of secondary emissions (K on Fig. III-1) are aqueous discharges from the three caustic scrubbers, the sulfuric acid drying column, and the dryer. Another potential source is the incineration of heavies from carbon tetrachloride distillation.

C. PROCESS VARIATIONS

Inert gases entering the process must be purged, causing losses of VOC. Variations in purity of feed materials therefore will have considerable impact on process emissions.

Variation in reaction conditions and in amounts of methyl chloride recycled to the chlorination reactor changes product yield ratios and therefore changes relative amounts of methylene chloride, chloroform, and carbon tetrachloride emitted during storage and loading.

D. REFERENCES*

1. D. W. F. Hardie, "Chlorocarbons and Chlorohydrocarbons," pp. 105--106 in Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 5, 2d ed., edited by A. Standen et al., Wiley-Interscience, New York, 1964.

2. Monsanto Research Corp., Dayton, Ohio, and Research Triangle Institute, Research Triangle Park, NC, Chapter 6. The Industrial Organic Chemicals Industry, Part I, p. 6-405 (nd).

3. F. A. Lowenheim and M. K. Moran, "Methyl Chloride -- Methylene Dichloride," pp. 530--532 in Faith, Keyes, and Clark's Industrial Chemicals, 4th ed., Wiley-Interscience, New York, 1975.

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IV. EMISSIONS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere participate in photochemical reactions producting ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Sections 111 or 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation. It should be noted that, although methylene chloride is included in VOC emission totals in this report, it does not, based on current research data, participate in ozone-forming reactions to an appreciable extent.

A. MODEL PLANT*

The total chloromethane capacity for the model plant was selected to be 200,000 Mg/yr. This capacity was selected because the only domestic facility based completely on the chlorination of methane, the Dow plant at Freeport, TX, is reported to have a capacity of about 200,000 Mg/yr. The percentages of total capacity for individual products were selected to be 20% methyl chloride, 45% methylene chloride, 25% chloroform, and 10% carbon tetrachloride. This product mix requires that methyl chloride be recycled for additional chlorination. About 171,000 Mg of by-product hydrogen chloride is generated per year for this product mix. Typical storage of raw materials, intermediates, and products was selected according to these percentages of individual products. The model plant was assumed to operate 8760 hr annually.**

The model methane chlorination process shown in Fig. III-1 fits today's engineering and manufacturing technology. The number of valves, pumps, and compressors is typical for a plant of this type. Characteristics of the model plant important to air dispersion are shown in Appendix B.

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*See page I-2 for a discussion of model plants.

**Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations the error introduced by assuming continuous operation is negligible.

B. SOURCES AND EMISSIONS

The process emissions for the methane chlorination process described in this report are based on the emissions reported[1] in response to EPA's requests for information, on the emission inventory questionnaire filed by Dow with the State of Texas, and comments furnished in response to the draft of this report.[2].

Sources and emission rates for the methane chlorination process for the product mix stated above are summarized in Table IV-1. Variation in reaction conditions and in amounts of methyl chloride recycled for further chlorination changes the co-product yield ratios and therefore changes the relative amounts of storage and loading emissions for the individual products.

1. Process Emissions

a. Recycled-Methane Inert-Gas Purge Vent -- Inert gases enter the process with feeds to the chlorination chamber and will remain with the unreacted methane throughout the methane purification procedure. A portion of the recycled methane stream is vented to prevent a buildup of inert gases, causing a loss of VOC (Vent A, Fig. III-1). From information supplied by a producer,[1] the non-methane VOC emissions resulting from this inert-gas purge were calculated to be 2.10 kg of chloromethanes per Mg of total chloromethanes capacity. The temperature of the vented gases is approximately 30°C.[1] The composition of the vented gases is shown in Table IV-2. Calculations based on the amount of inert gases reported and on chlorine requirements for a 200,000-Mg/yr capacity plant producing the product mix selected for the model plant show that very high purity (99.9 wt % pure) chlorine is being used. Decreases in chlorine purity would increase the amount of inert-gas and VOC emissions.

b. Drying-Bed Regeneration Vent -- The drying bed for the recycled methane must be regenerated periodically (Vent B, Fig. III-1). This regeneration results in VOC emissions of about 0.052 kg per Mg of total chloromethanes produced as calculated from information supplied by a producer. The composition of gases vented at the source was reported as 67 mole % methyl chloride and 33 mole % methane.[1]

Table IV-1. Total Uncontrolled[a] Nonmethane VOC Emissions for Model Plant Producing Chloromethanes by Methane Chlorination Process

Source	Stream Designation (Fig.III-2)	Total VOC Emission[b] Ratio[c] (kg/Mg)	Total VOC Emission[b] Rate (kg/hr)
Recycled-methane inert-gas purge vent[d]	A	2.10	48.0
In-process storage	D	0.63	14.5
Drying-bed regeneration vent[e]	B	0.052	1.19
Distillation-area emergency inert-gas vent[d]	C	0.20	4.48
Product storage	D	0.92	20.9
Handling[e]	D	0.36	8.33
Fugitive	F	1.74	39.7
Secondary[d,f]	K	0.13	2.99
Total		6.13	140

[a] Uncontrolled emissions are emissions from process using no additional control devices other than those necessary for economical operation.

[b] Emissions include methyl chloride, methylene chloride, chloroform, and carbon tetrachloride. Methane emissions are not included.

[c] kg of emissions per Mg of chloromethanes produced.

[d] See ref 1.

[e] See ref 2.

[f] See ref 5.

Table IV-2. Characteristics of Emissions from Recycled-Methane Inert-Gas Purge Vent from Methane Chlorination Process[a]

Constituent	Quantity (mole %)	Emission Ratio[b] (kg/Mg)
Oxygen	0.15	0.013
Nitrogen	18.94	1.45
Methane	65.91	2.89
Methyl chloride	14.78	2.04
Methylene chloride	0.22	0.051
Chloroform	0.01	0.0033
Carbon tetrachloride	<0.01	<0.0042

[a] See ref. 1.

[b] kg of emissions per Mg of total chloromethanes capacity.

c. Distillation-Area Emergency Inert-Gas Vent -- Process emissions result from emergency venting (safety relief venting) of distillation-area equipment (Vent C, Fig. III-1). These emissions can be vented back into the system. VOC emissions during the emergency venting were calculated from information supplied by a producer to be 0.20 kg per Mg of total chloromethanes capacity.[2] The composition of uncontrolled emissions from this source was reported as 40 mole % chlorine, 34.6 mole % hydrogen chloride, 22.4 mole % chlorinated VOC and 3 mole % air.

2. Fugitive Emissions

Process pumps, valves, flanges, and compressors are potential sources of fugitive emissions. The model plant is estimated to have 80 pumps (including spares), 2000 process valves including 70 relief valves, and a compressor. The factors shown in Appendix C were used to determine the fugitive emissions listed in Table IV-1.

3. Storage and Handling Emissions

Emissions result from storage and handling of methylene chloride, chloroform, and carbon tetrachloride. No methyl chloride storage and handling emissions are projected, because methyl chloride is stored in pressure vessels. The sources of storage and handling emissions for the model plant are shown on the flow diagram in Fig. III-1 (Source D). Storage tank conditions for the model plant are given in Table IV-3. The uncontrolled storage emissions in Table IV-1 were calculated with the emission equations from AP-42[3] and on the assumptions of a diurnal temperature variation of 12°C and of fixed-roof tanks that on the average are half full. However, breathing losses were divided by 4 to account for recent evidence indicating that the AP-42 breathing loss equation overestimates emissions.[4]

Emissions from loading methylene chloride, chloroform, and carbon tetrachloride product into tank cars and trucks were calculated with the equations from AP-42.[3] Submerged loading into clean tank cars and trucks was assumed for the emission calculations. Another assumption was that the loading device for methyl chloride has a vapor return loop and therefore creates no emissions except for emissions that would be classified as fugitive in nature.

Table IV-3. Storage Requirements for Model Plant Producing Chloromethanes by Chlorination of Methane Process

Stored Material	Number of Tanks	Tank Size (m^3)	Turnovers Per Year	Bulk Liquid Temperature (°C)
Methyl chloride	1	1890	23	20
Crude methylene chloride--chloroform--carbon tetrachloride	1	757	6*	35
Methylene chloride	2	227	150	30
Chloroform	2	114	147	35
Carbon tetrachloride	2	38	166	35
Methylene chloride	1	3780	18	20
Chloroform	1	1510	22	20
Carbon tetrachloride	1	757	17	20

*Surge tank operated at nearly constant level.

4. Secondary Emissions

Secondary VOC emissions can result from the handling and disposal of process waste liquid. For the model plant the potential sources of secondary emissions from waste liquid are indicated on the flow diagram, Fig. III-1 (Source K). These liquid streams are waste caustic from the scrubbers on the methyl chloride and recycle methane streams and the crude chloromethanes neutralizer, sulfuric acid from the dryer on the methyl chloride product stream, the high-density salt solution discharge from the crude chloromethane dryer, and heavies from the carbon tetrachloride distillation column. The waste caustic and salt solutions from the dryer are discharged from the process as aqueous waste and the sulfuric acid is stored for reclamation or sales. The heavies from carbon tetrachloride distillation are incinerated. The secondary emissions given for the model plant in Table IV-1 were calculated based on the chloromethanes content reported for total wastewater discharges from a methane chlorination process[1] and the chloromethanes content of sulfuric acid waste from a process based on both the methanol hydrochlorination and methyl chloride chlorination and the methane chlorination processes.[5]

C. REFERENCES*

1. J. Beale, Dow Chemical U.S.A., Midland, MI, letter dated Apr. 28, 1978, to L. Evans, EPA, concerning Dow facility at Freeport, TX.

2. S. L. Arnold, Dow Chemical U.S.A. Midland, MI, letter dated July 31, 1979, to David R. Patrick, EPA.

3. C. C. Masser, "Storage of Petroleum Liquids," pp. 4.3-2 to 4.3-11 in Supplement No. 7 for Compilation of Air Pollutant Emission Factors, AP-42, 2d ed., EPA, Research Triangle Park, NC (April 1977).

4. E. C. Pularski, TRW, Inc., letter dated May 30, 1979, to Richard Burr, EPA.

5. J. J. Muthig, Allied Chemical, Moundsville, WV, letter dated Mar. 31, 1978, to D. R. Goodwin, EPA.

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V. APPLICABLE CONTROL SYSTEMS

The controls described in this section relate to the manufacture of chloromethanes by the methane chlorination process.

A. EMISSION CONTROLS FOR MODEL PLANT

1. Process Emissions

a. Recycled-Methane Inert-Gas Purge Vent -- Emissions resulting from venting of inert gases from the recycled-methane stream (Vent A, Fig. III-1) constitute about 34% of the total model-plant uncontrolled emissions. No controls are reported by industry for this stream. Several alternatives were considered for control of these emissions. Carbon adsorption was determined to be an impractical control alternative, because methyl chloride, the major nonmethane VOC in the vented gases, is highly volatile at practical operating temperatures and pressures and therefore has a very low loading factor on carbon. Also, streams containing high concentrations of VOC must be diluted with additional inert gases to prevent large temperature increases in the carbon bed. Both factors would contribute to a high unit cost per unit of VOC recovered. The inert gas composition of feed materials to the reactor is a major determinant in the total amount of VOC emitted. Use of higher purity raw materials was not considered as a control option, because the model plant is assumed to use purified (liquified and revaporized) chlorine.

Thermal oxidation also was considered not to be a sufficiently feasible option to justify a detailed study. Formation of hydrogen chloride during oxidation of chlorinated VOC would necessitate corrosion-resistant materials of construction and the addition of an acid-gas scrubber for the vent gases from the oxidizer. Both these factors would contribute to high capital and operating costs. If, however, a producer has a thermal oxidizer operating on other chlorinated wastes, then the addition of this emission stream for control may be feasible.

The control option selected for detailed study was an absorption system utilizing chloroform drawn from storage, chilled, and used as an absorbent. Absorption in a less volatile hydrocarbon is a common method for the recovery of light hydrocarbons. For example, the methane chlorination model process uses absorption, as is shown in Fig. III-1, to separate chloromethanes from other gases exiting the reactor. An absorption system could be used for control of the recycled-methane inert-gas purge vent and in-process storage tank emissions. The control of these combined sources by a single absorber is the conceptual approach used for the model plant. The absorbent and absorbed materials can be returned to the process for recovery.

The absorber system for combined recycled-methane inert-gas purge vent and in-process storage emissions is a preliminary design for cost estimating purposes per the standard design methods described by Treybal.[1] The design has not been optimized. The design parameters with the greatest effect on control efficiency are final gas temperature and pressure due to their effects on the vapor pressure of the VOC components and the composition of the gaseous stream vented from the absorber. As a general relationship the total VOC emitted from the absorber will vary directly with the absolute pressure of the system. An absorber designed to operate at -40°C and at a pressure of about 2×10^5 Pa will reduce the model-plant uncontrolled emissions from the combined recycled-methane inert-purge vent and in-process storage sources by about 92% as shown for the model plant in Table V-1. A reduction of about 72% would be achieved if the operating temperature were increased to -29°C.[2]

b. Drying-Bed Regeneration Vent -- Emissions resulting from regeneration of the methyl chloride drying bed are uncontrolled because they constitute only about 1% of total model-plant uncontrolled emissions and are intermittent. Emissions from this vent were not included for control by the absorption system because moisture from the regeneration of the drying bed would cause difficulties in recycling the recovered material to the process.

c. Distillation-Area Emergency Inert-Gas Purge Vent -- Emissions resulting from emergency venting of distillation-area equipment remain uncontrolled because they constitute only about 1% of the total uncontrolled model plant emissions and are intermittent. These emissions were not included for control by the absorption system discussed above because hydrogen chloride is reported to be included in the emissions.[3] Special materials of construction would be required for the absorption system if these emissions had been included for control.

Table V-1. Controlled VOC Emissions for Model Plants Producing Chloromethanes by Methane Chlorination

Source	Stream Designation (Fig. III-1)	Control Device or Technique	Reduction (%)	VOC Emissions Ratio[a] (kg/mg)	VOC Emissions Rate (kg/hr)
Recycled-methane inert-gas purge vent[b]	A	Absorber	92	0.22	5.0
In-process storage[b]	D				
Drying-bed regeneration vent[c]	B	None		0.052	1.19
Distillation-area emergency[c] inert-gas vent	C	None		0.20	4.48
Product storage	D	Condensation	80.0	0.18	4.18
Handling[c]	D	None		0.36	8.33
Fugitive	F	Detection and correction of leaks	67.5	0.57	12.9
Secondary[c]	K	None		0.13	2.99
Total				1.71	39.1

[a] kg of emissions per Mg of chloromethanes produced.

[b] Combined for control by absorber.

[c] Uncontrolled.

Also, the highly intermittent nature of these emissions could cause difficulties in sizing a control device.

2. Fugitive Emissions

Control for fugitive sources is discussed in a separate EPA report.[4] The controlled fugitive emissions shown in Table V-1 are based on the factors given in Appendix C and on the assumption that any major leaks would be detected and repaired.

3. Storage

Storage emissions can be controlled by condensation or absorption. For the model plant it is assumed that in-process storage emissions are combined with emissions from the inert-gas purge vent for control and that condensation is used to control product storage emissions. Total SOCMI VOC storage emissions are covered in a separate EPA report.[5]

4. Handling Emissions

No unique handling controls are known to be practiced by industry. Therefore the handling emissions for the controlled model plant are the same as for the uncontrolled model plant.

5. Secondary Emissions

Secondary sources contribute about 2% of the total uncontrolled model-plant emissions. No unique secondary emissions control techniques are known to be practiced by industry. Therefore the secondary emissions for the controlled model plant are the same as for the uncontrolled model plant. Emissions from secondary sources are discussed in a separate EPA report.[6]

B. REFERENCES*

1. R. E. Treybal, Mass-Transfer Operations, chaps. 6 and 8, McGraw-Hill, New York, 1955.
2. S. L. Arnold, Dow Chemical U.S.A., Midland, MI, letter to David L. Patrick, EPA, July 31, 1979.
3. J. Beale, Dow Chemical U.S.A., Midland, MI, letter to L. Evans, EPA, April 28, 1978.
4. D. G. Erikson and V. Kalcevic, IT Enviroscience, Inc., Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).
5. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, NC).
6. J. Cudahy and R. L. Standifer, IT Enviroscience, Inc., Secondary Emissions (June 1980) (EPA/ESED report, Research Triangle Park, NC).

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VI. IMPACT ANALYSIS

A. ENVIRONMENTAL AND ENERGY IMPACTS

Table VI-1 shows the environmental impact of reducing VOC emissions by application of the indicated control systems for the 200,000-Mg/yr capacity model plant using the methane chlorination process for production of chloromethanes. Use of these control devices or techniques results in the reduction of VOC emissions by 885 Mg/yr for the model plant. Individual impacts are discussed below.

1. Model Plant

a. Recycled-Methane Inert-Gas Purge Vent and In-Process Storage -- An absorber for control of combined emissions from the recycled-methane inert-gas purge vent and in-process storage sources reduced model-plant VOC emissions by 504 Mg/yr. The absorber uses electric power, but the energy required is small.

b. Other Emissions (Other Process, Other Storage, Handling, Fugitive, and Secondary) -- Control methods described for these sources are a condenser for product storage sources and correction of leaks for fugitive emissions. Application of these systems results in a reduction in VOC emissions of 381 Mg/yr for the model plant. No control devices are described for process sources other than the recycled methane inert-gas purge vent or for handling and secondary sources.

2. Industry Emissions

Only one producer (Dow at Freeport, TX) is known to operate a chloromethane facility based solely on the methane chlorination process. Two producers (Vulcan at Wichita, KS, and Allied at Moundsville, WV) operate chloromethane production facilities that are based at least in part on methane chlorination (approximately 15,000 Mg/yr total methane capacity), but most of the capacity at these facilities is based on methanol hydrochlorination and methyl chloride chlorination. Therefore the Dow 200,000-Mg/yr capacity chloromethanes plant represents the methane chlorination industry and was the basis for the model plant capacity as described previously in this report. Because the actual production rate of the single facility is proprietary information the model capacity was assumed to be the industry production rate. The methane chlorination industry emissions were

Table VI-1. Environmental Impact of Controlled VOC Emissions for 200,000-Mg/yr Methane Chlorination Model Plant

Emission Source	Stream Designation (Fig. III-1)	Control Device or Technique	Emission Reductio	
			(%)	(Mg/yr)
Recycled-methane inert-gas purge vent[b]	A	Absorber	92	504
In-process storage[b]	D			
Drying-bed regeneration vent	B	None		
Distillation-area emergency inert-gas vent	C	None		
Product storage	D	Condenser	80	146
Handling	D	None		
Fugitive	F	Detection and correction of leaks	67.5	235
Secondary	K	None		
Total				885

[a] Annual reduction is based on 8760 hr of operation. Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operat on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation is negligible.

[b] Combined for control.

determined from actual process, storage, and handling emissions as reported by Dow;[1] from the secondary emissions as determined from the chloromethanes content in the wastewater discharged at the Dow plant[1] and from the chloromethanes content in spent sulfuric acid reported by Allied;[2] and from the estimate that fugitive emissions were uncontrolled and similar to those from the uncontrolled model plant. The industry emissions are listed below:

Source	Emissions (kg/hr)
Process	53.7
Storage	2.9
Handling	23.4
Secondary	3.0
Fugitive	39.7
Total	122.7

Storage emissions were calculated from reported data[1] to be about 94% controlled by condensation. No other control devices were reported.

B. CONTROL COST IMPACT

This section gives estimated costs and cost-effectiveness data for control of VOC emissions resulting from the production of chloromethanes by the methane chlorination process. Details of the model plant (Fig. III-1) are given in Sects. III and IV.

Capital cost estimates represent the total investment required for purchase and installation of all equipment and material needed for a complete emission control system performing as defined for a new plant at a typical location. These estimates do not include the cost of research and development, of land acquisition, or of chloromethanes production lost during installation or startup. Also, the potential need for additional chloroform distillation capacity is not considered.

Bases for the annual cost estimates for the control alternatives include utilities, raw materials, maintenance supplies and labor, recovery credits, capital charges, and miscellaneous recurring costs such as taxes, insurance, and administrative overhead. (Manpower costs are minimal and therefore are not included.) The cost factors that were used are itemized in Table VI-2. Emission recovery credits are based on the raw material value of the material being recovered. Annual costs are for a 1-year period beginning December 1979.

1. Process Emissions

The major source of emissions from the methane chlorination process is the recycled-methane inert-gas purge vent. These emissions and those from in-process storage are controlled with an absorption system. The cost estimate for the control system is as follows:

Total installed capital cost	$130,000
Utilities	$1,200
Fixed costs	$38,000
Recovery credits	($125,000)
Net annual savings	($85,800)
Emission reduction	504 Mg/yr; 92%
Cost effectiveness (per Mg)	($170) (savings)

The absorbent material for the VOC emissions is chloroform from the process, and the recovery credit is based on the value of the net recovery of methyl chloride, methylene chloride, chloroform, and carbon tetrachloride, which are recycled to the process. Cost effectiveness is the net annual cost divided by the Mg/yr emission reduction.

Other process emissions, which originate at the drying-bed regeneration and distillation-area emergency inert-gas vents, constitute only about 4% of the total uncontrolled model-plant emissions and remain uncontrolled.

2. Storage and Handling Sources

Another EPA report covers storage emissions and their applicable controls for all the synthetic organic chemicals manufacturing industry.[3]

a. In-Process Storage -- In-process storage sources can be controlled in combination with the absorption system discussed previously or by use of chilled condensers.

Table VI-2. Cost Factors Used in Computing Annual Costs

Item	Factor
Utilities	
Electricity	\$8.33/GJ
Cooling water	\$0.026/m^3
Operating time	8760 hr/yr
Operating labor	Minor; not considered
Fixed costs	
Maintenance labor, 6%	29% of installed cost
Capital recovery, 18% (10 yr life @ 12% interest)	
Taxes, insurance, administration, 5%	
Recovery credits[a]	
Methyl chloride	\$243/Mg
Methylene chloride	\$265/Mg
Chloroform	\$278/Mg
Carbon tetrachloride	\$284/Mg

[a] Based on raw material costs for chlorine in "Current Prices of Chemicals and Related Materials," Chemical Marketing Reporter, April 1, 1980, and a methane cost of \$0.07/1000 l.

b. Product Storage -- The systems for control of product storage emissions include the use of chilled condensers.

c. Handling -- No system has been defined for control of the emissions from handling sources.

3. Fugitive Sources

A control system for fugitive sources is defined in Appendix C. Another report describes fugitive emissions and their applicable controls for the synthetic organic chemicals manufacturing industry.[4]

4. Secondary Sources

No control system has been identified for controlling the secondary emissions from the process. Another report covers secondary emissions and their applicable controls for the synthetic organic chemicals manufacturing industry.[5]

C. REFERENCES*

1. J. Beale, Dow Chemical, U.S.A., Midland, MI, letter to L. Evans, EPA, Apr. 28, 1978.

2. J. J. Muthig, Allied Chemical, Moundsville, WV, letter to D. R. Goodwin, EPA, Mar. 31, 1978.

3. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, NC).

4. D. Erikson and V. Kalcevic, IT Enviroscience, Inc., Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

5. J. Cudahy and R. L. Standifer, IT Enviroscience, Inc., Secondary Emissions (June 1980) (EPA/ESED report, Research Triangle Park, NC).

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*A reference located at the end of a paragraph usually refers to the entire paragraph. If another reference relates to certain portions of the paragraph, the reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VII. SUMMARY

The four chloromethanes -- methyl chloride, methylene chloride, chloroform, and carbon tetrachloride -- are produced by the chlorination of methane. Projections for anticipated usage patterns for the chloromethanes as detailed in Sect. II indicate above-average growth in methylene chloride and chloroform use, nearly static usage for methyl chloride, and severe declines in demand for carbon tetrachloride. No plans are known for new chloromethanes production facilities based on the methane chlorination process. Dow reportedly planned to increase its production capacity by late 1979.[1]

The major emission sources for the methane chlorination model plant are the recycled-methane inert-gas purge vent, in-process storage, final-product storage, and handling. The first two sources can be combined for potential control with an absorber, which results in about 92% control. The final-product storage can be controlled by use of a chilled condenser. No unique control systems are proposed for the handling sources.

The methanol hydrochlorination and methyl chloride chlorination processes, which produce three of the chloromethanes (methyl chloride, methylene chloride, and chloroform), are described in another report[2] to have estimated current industry emissions of 252 kg/hr. Based on a 1979 production projection of about 565,000 Mg, the industry using these processes therefore is estimated to have an emission ratio of 3.9 kg of VOC per Mg of chloromethanes produced. By comparison the methane chlorination process described in this report has current industry emissions of 122.7 kg/hr for an estimated emission ratio of 5.4 kg of VOC per Mg of chloromethanes produced.

Existing plant considerations are discussed in Appendix D.

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[1] J. C. Blackford, "CEH Marketing Report on Methanol," pp. 674.5022Z--674.5023G in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (August 1977).

[2] F. D. Hobbs and C. W. Stuewe, IT Enviroscience, Inc., Chloromethanes Manufactured by Methanol Hydrochlorination and Methyl Chloride Chlorination (November 1980) (EPA/ESED report, Research Triangle Park, NC).

APPENDIX A

Table A-1. Physical Properties of Chloromethane Compounds

Chemical name	Chloromethane[a]	Dichloromethane[b]	Chloroform[a]	Carbon tetrachloride[c]
Synonym	Methyl chloride	Methylene chloride, methylene dichloride	Trichloromethane	Tetrachloromethane, perchloromethane, methane tetrachloride
Molecular formula	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
Molecular weight	50.49	84.93	119.31	153.82
Physical state	Gas	Liquid	Liquid	Liquid
Vapor pressure	5.0 atm at 22°C[d]	435.8 mm Hg at 25 °C	200 mm Hg at 25.9°C	115.2 mm Hg at 25°C
Vapor specific gravity	1.78	2.93	4.12	5.32
Boiling point	-24.2°C	40°C	61.26°C	76.54°C
Melting point	-97.73°C	-95.1°C	-63.5°C	-22.99°C
Density	0.9159 g/ml at 20°C/4°C	1.3266 g/ml at 20°C/4°C	1.49845 g/ml at 15°C	1.5940 g/ml at 20°C/4°C
Water solubility	4.9 g/liter	Slight	8.0 g/liter	Insoluble

[a] J. Dorigan *et al.*, "Scoring of Organic Air Pollutants. Chemistry, Production, and Toxicity of Selected Synthetic Organic Chemicals (Chemicals F-N)," p. AIII-174 in MTR-7428, Rev. 1, Appendix III, MITRE Corp., METREK Division (September 1976).

[b] *Ibid.*, p. AIII-186.

[c] *Ibid.*, p. AI-222.

[d] *Perry's Chemical Engineers' Handbook*, 4th ed., p. 3-60, McGraw-Hill, New York, 1963.

APPENDIX B

AIR-DISPERSION PARAMETERS

Table B-1. Air-Dispersion Parameters for Uncontrolled and Controlled Model Plant Using Methane Chlorination Process (200,000 Mg/yr)

Source[a]	Emission Rate (g/sec)	Tank Height (m)	Tank Diameter (m)	Stack Height (m)	Stack Diameter (m)	Discharge Temperature (K)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
				Uncontrolled Emissions				
Recycled-methane inert-gas purge vent	13.3			11.0	0.025	303	4.4×10^{-2}	90
Crude storage	0.79	9.8	9.9			308		
Methylene chloride day tanks (2)	1.07	7.3	6.3			303		
Chloroform day tanks (2)	0.43	7.3	4.5			308		
Carbon tetrachloride day tanks (2)	0.12	2.4	4.5			308		
Drying-bed regeneration vent	0.33			11.0	0.025	393	2.8×10^{-4}	0.57
Distillation-area emergency inert-gas vent	1.24			11.0	0.025	308	4.6×10^{-4}	0.93
Methylene chloride product storage	4.13	12.2	19.9			293		
Chloroform product storage	1.30	12.2	12.6			293		
Carbon tetrachloride product storage	0.39	9.8	9.9			293		
Handling	2.31							
Fugitive[b]	11.0							
Secondary	0.83							
				Controlled Emissions				
Absorber	1.78			11.0	0.025	233	3.7×10^{-2}	75
Drying-bed regeneration vent[c]	0.33			11.0	0.025	393	2.8×10^{-4}	0.57
Distillation-area emergency inert-gas vent[c]	1.24			11.0	0.025	308		
Product storage condenser	1.16							
Handling[c]	2.31							
Fugitive[b]	3.58							
Secondary[c]	0.83							

[a] One except where indicated otherwise.

[b] Distributed over an area of about 50 X 100 m.

[c] Will reamin uncontrolled.

APPENDIX C

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX D

EXISTING PLANT CONSIDERATIONS

A. CURRENT INDUSTRY

Only four chloromethane producing facilities——Allied at Moundsville, WV; Dow at Freeport, TX, and Pittsburg, CA; and Vulcan at Wichita, KS——use methane as a feed material. The Allied and Vulcan facilities primarily utilize the methanol hydrochlorination and methyl chloride chlorination processes; methane chlorination accounts for only about 5% of the Allied capacity and 10% of the Vulcan capacity.[1],[2] The Dow plant at Pittsburg, CA, may utilize methane as a feed to a chlorinolysis process. Therefore the single facility known to utilize the methane chlorination process exclusively is the Dow plant at Freeport, TX. That plant accounts for about 15% of the total chloromethanes industry capacity. An increase in capacity was scheduled to be brought on-stream late in 1979 at that plant.[3]

Dow reports use of a condenser for control of storage emissions and scrubbers for control of hydrogen chloride emissions.[4]

B. RETROFITTING CONTROLS

The primary difficulty associated with retrofitting may be in finding space to fit the control device into existing plant layout. Because of costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems than to install a control system during construction of a new plant.

The absorption device conceptualized for control of combined emissions from the inert-gas purge vent and in-process storage vents could be especially difficult to retrofit. Influence of the control device on equipment, such as chloroform distillation capacity, should be considered before this control device is considered for use.

C. REFERENCES*

1. Personal communication between F. D. Hobbs, IT Enviroscience, Inc., and D. Denoon, Allied Chemical, Moundsville, WV, July 25, 1978.

2. Personal communication between F. D. Hobbs, IT Enviroscience, Inc., and T. A. Robinson, Vulcan Materials Company, Wichita, KS, July 28, 1978.

3. T. F. Killiea, "CEH Product Review on Chlorinated Methanes," pp. 625.2030A - 635.2031G in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (April 1979)

4. J. Beale, Dow Chemical U.S.A., letter to L. Evans, EPA, April 28, 1978.

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

APPENDIX E

COST ESTIMATE SAMPLE CALCULATIONS

This appendix contains sample calculations showing how costs presented in this report were estimated.

The accuracy of an estimate is a function of the degree of data available when the estimate was made. Figure E-1 illustrates this relationship. A contingency allowance as indicated on this chart has been included in the estimated costs to cover the undefined scope of the project.

Capital costs given in this report are based on a screening study, as indicated by Fig. E-1, based on general design criteria, block flowsheets, approximate material balances, and data on general equipment requirements. These costs have an accuracy range of +30% to -23%, depending on the reliability of the data, and provide an acceptable basis to determine the most cost-effective alternate within the limits of accuracy indicated.

This example is based on use of an absorption system operated at -40°F, with refrigerated chloroform as the absorbent, to control the emissions from the recycled-methane inert-gas purge vent and from the in-process storage vents. The absorption system consists of a pump for metering the chloroform, a refrigeration unit for cooling the chloroform, an absorption column, and a compressor to raise the pressure of the emissions from in-process storage to 2 atm., the operating pressure of the absorption column. Capital costs for all components were estimated from IT Enviroscience installed cost data. Cost data compiled from previous years were adjusted to a December 1979 basis.

Total installed capital cost = $130,000

The annual fixed costs are 29% of the installed cost (see Table VI-6):

0.29 X $130,000 = $38,000 (rounded).

The utility costs are calculated as follows (see Table VI-6):

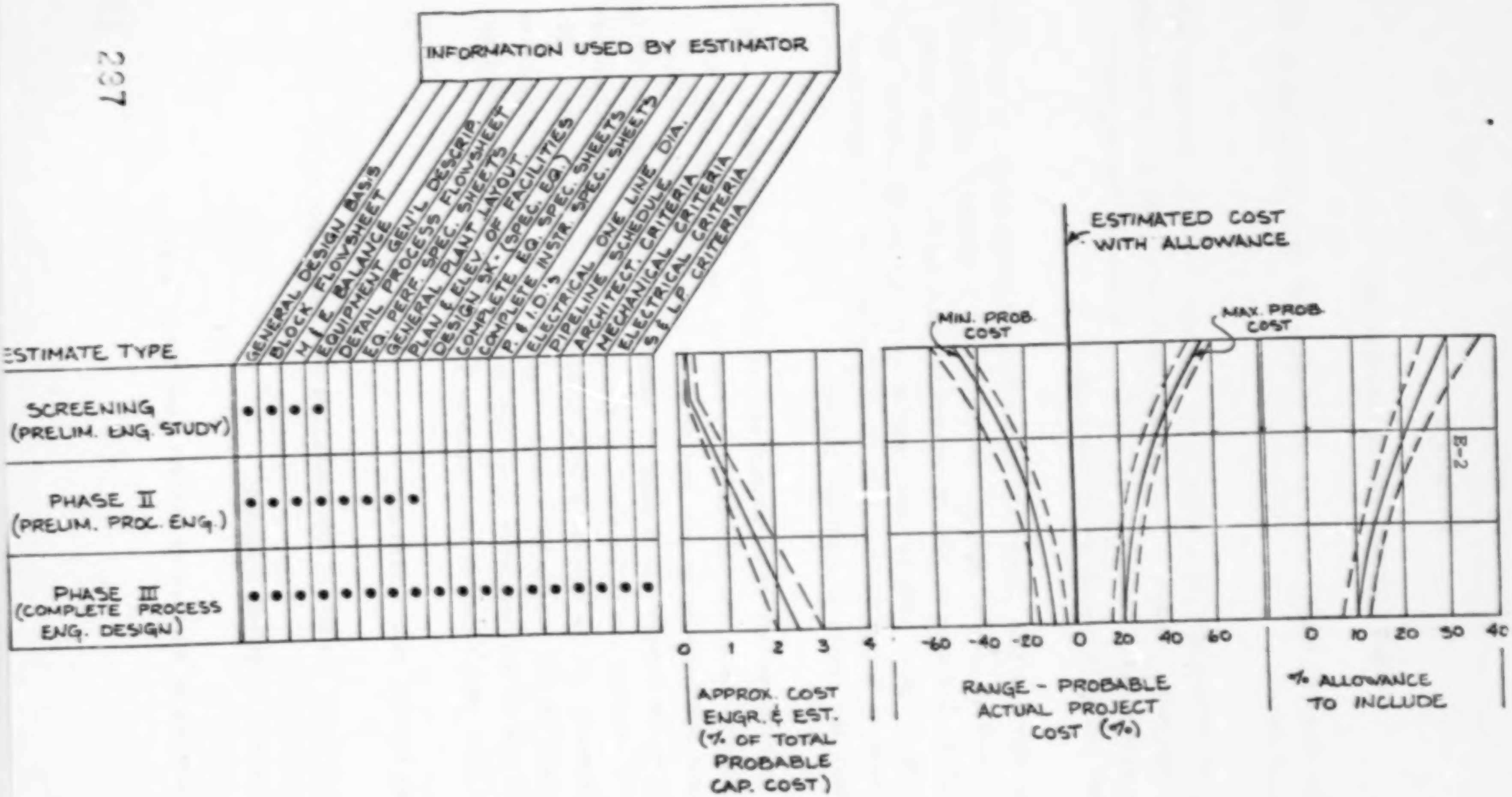

Fig. E-1. Precision of Capital Cost Estimates

LATEST REVISION - 5/2/77

Electricity useage is estimated as 3 kWh per hour

$$\frac{3\ \text{kWh}}{\text{hr}} \times \frac{\$0.03}{\text{kWh}} \times \frac{8760\ \text{hr}}{\text{yr}} = \$800/\text{yr (rounded)}$$

Cooling water required is estimated as 8 gpm

$$\frac{8\ \text{gal}}{\text{min}} \times \frac{\$0.10}{1000\ \text{gal}} \times \frac{60\ \text{min}}{\text{hr}} \times \frac{8760\ \text{hr}}{\text{yr}} = \$400/\text{yr (rounded)}$$

Total utility costs = \$800 + \$400 = \$1,200

The recovery credit is calculated as follows (see Table VI-6):

$$\text{Methyl chloride} = \frac{339\ \text{Mg}}{\text{yr}} \times \frac{\$243}{\text{mg}} = \$82{,}400/\text{yr}$$

$$\text{Methylene chloride} = \frac{129\ \text{Mg}}{\text{yr}} \times \frac{\$265}{\text{Mg}} = \$34{,}200/\text{yr}$$

$$\text{Chloroform} = \frac{11\ \text{mg}}{\text{yr}} \times \frac{\$278}{\text{Mg}} = \$3{,}100/\text{yr}$$

$$\text{Carbon tetrachloride} = \frac{25\ \text{Mg}}{\text{yr}} \times \frac{\$284}{\text{Mg}} = \$7{,}100/\text{yr}$$

Totals (VOC = 504 Mg/y) \$130,000/yr (rounded)

Estimated cost of reprocessing chloroform used as absorbent = \$1.20/Mg

$$\frac{4200\ \text{Mg}}{\text{yr}} \times \frac{\$1.20}{\text{Mg}} = \$5{,}000/\text{yr}$$

Net recovery credit = \$130,000/yr—\$5,000/yr = \$125,000/hr.

Summary of Annual Costs

Fixed Costs = $ 38,000

Utility Costs = 1,200

Recovery Credit = (125,000)

Net Annual Savings = (85,800)

Emission Reduction = 504 Mg/yr

$$\text{Cost effectiveness} = \frac{(\$85{,}800)}{504\ \text{Mg}} = (\$170/\text{Mg})\ (\text{savings})$$

REPORT 6

CHLOROMETHANES MANUFACTURED BY METHANOL HYDROCHLORINATION AND METHYL CHLORIDE CHLORINATION PROCESSES

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November 1980

This report contains certain information which has been extracted from the Chemical Economics Handbook, Stanford Research Institute. Wherever used, it has been so noted. The proprietary data rights which reside with Stanford Research Institute must be recognized with any use of this material.

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870×10^{-6}
Joule (J)	British thermal unit (Btu)	9.480×10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531×10^{1}
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643×10^{2}
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585×10^{4}
Watt (W)	Horsepower (electric) (hp)	1.340×10^{-3}
Meter (m)	Inch (in.)	3.937×10^{1}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778×10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^{9}	1 Gg = 1 X 10^{9} grams
M	mega	10^{6}	1 Mg = 1 X 10^{6} grams
k	kilo	10^{3}	1 km = 1 X 10^{3} meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

II. INDUSTRY DESCRIPTION

A. REASON FOR SELECTION

Four volatile organic compounds (VOC) -- methyl chloride, methylene chloride, chloroform, and carbon tetrachloride -- comprise the group commonly referred to as chloromethanes. These compounds were selected for study because preliminary estimates indicated that their production causes relatively high VOC emissions.

There are four processes by which chloromethanes are produced either as co-products or as individual products. One of the processes also results in the production of perchloroethylene as a co-product. This report describes the processes of methanol hydrochlorination, which yields methyl chloride, and methyl chloride chlorination, which yields methylene chloride and chloroform. The two processes are combined for consideration because industry generally utilizes them in combination. Small amounts of carbon tetrachloride are produced as a by-product in the methyl chloride chlorination, but it is not general industry practice to purify this carbon tetrachloride directly into product.

The process of methane chlorination, which produces all four chloromethanes, and the process of mixed hydrocarbon chlorinolysis, which produces carbon tetrachloride and perchloroethylene is covered by a separate report.[1]

B. METHYL CHLORIDE

1. General Description

Methyl chloride is a gas at ambient conditions but is handled commercially in liquid form (see Appendix A for pertinent physical properties). It is produced by methanol hydrochlorination or by methane chlorination. The predominant VOC emissions from its manufacture by the methanol hydrochlorination process are methyl chloride and methanol.

2. Usage and Growth

The end uses and expected growth rates of methyl chloride are given in Table II-1. The predominant use of methyl chloride is as an intermediate in the production of silicones and in the production of tetramethyllead, a gasoline additive. The expected increase in usage as an intermediate for silicone production combined

Table II-1. Methyl Chloride Usage and Growth[a]

End Use[b]	Production (%) 1977	Average Annual Growth (%)
Silicone intermediate	63	10—12
Tetramethyllead intermediate	18	-25
Butyl rubber (catalyst solvent)	8	3.5
Miscellaneous	11	NA[c]

[a] See refs 2 and 3.

[b] Amounts consumed as intermediates in continuous production of other chloromethanes not included.

[c] Not available.

with decreases in usage as an intermediate for tetramethyllead production, which is being restricted as a gasoline additive,[2] will result in nearly static production patterns for methyl chloride. Large amounts of the methyl chloride manufactured are not recovered as product but are further chlorinated to produce methylene chloride and chloroform. This usage is not included in the production and end-use statistics.[3]

The current domestic methyl chloride production capacity is reported to be about 283,000 Mg/yr,[3] with the 1979 production utilizing only about 72% of that capacity.[4] The annual growth in methyl chloride production is expected to remain static or at best to increase by 5% annually. Even at the 5% annual growth rate, production would reach only about 83% of capacity by 1982. There are no known plans for new methyl chloride production facilities.

3. Domestic Producers

There are ten domestic producers of methyl chloride operating 13 plants. Table II-2 lists the producers, locations, capacities, and processes in use; Fig. II-1 shows the plant locations. The Dow plant at Freeport, TX, produces methyl chloride by chlorination of methane. Allied uses hydrochlorination of methanol for about 95% of its production and uses chlorination of methane for the remaining production.[5] Vulcan operates two chloromethanes facilities at Wichita, KS. One is a recently constructed facility based completely on hydrochlorination of methanol, and the other (older) facility uses both hydrochlorination of methanol and chlorination of methane. Hydrochlorination of methanol accounts for about 90% of the total combined production.[6] All other manufacturers produce methyl chloride by hydrochlorination of methanol. The two Vulcan plants use all the methyl chloride they produce as an intermediate and therefore report no methyl chloride capacity as such. Allied, Diamond Shamrock, Dow, and Stauffer produce the higher chloromethanes in addition to methyl chloride. The ratios of co-products produced at these plants are flexible because the methyl chloride may be separated as product or may be further chlorinated to produce methylene chloride and chloroform. Continental, Dow Corning, Ethyl, General Electric, and Union Carbide produce only methyl chloride.

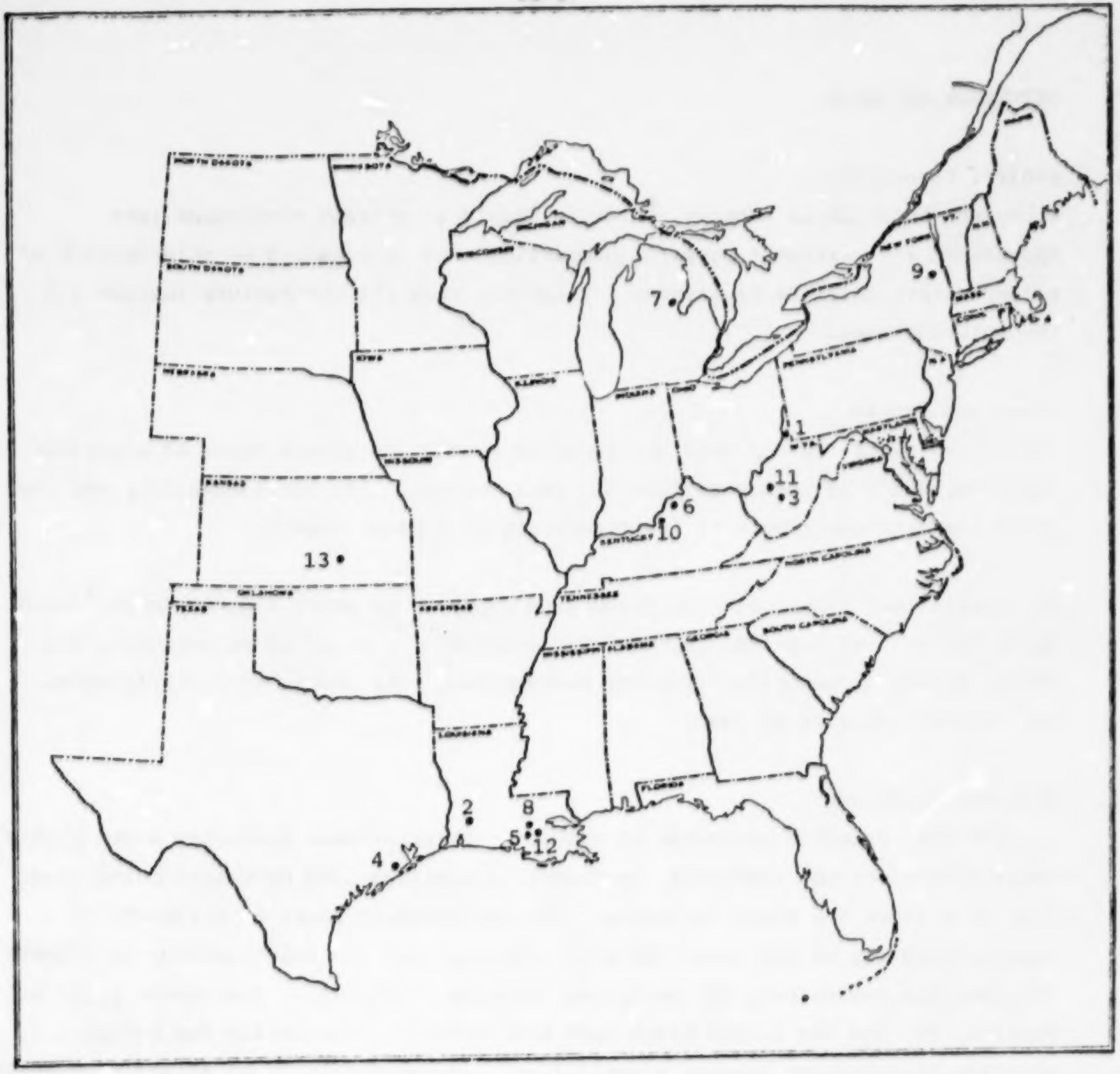
Table II-2. Methyl Chloride Capacity[a]

Plant	1977 Capacity ($\times 10^3$ Mg)	Process
Allied, Moundsville, WV	11[b]	Methanol hydrochlorination and methane chlorination
Continental, Westlake, LA	46	Methanol hydrochlorination
Diamond Shamrock, Belle, WV	11[b]	Methanol hydrochlorination
Dow, Freeport, TX	32[b]	Methane chlorination
Dow, Plaquemine, LA	68[b]	Methanol hydrochlorination
Dow Corning, Carrolton, KY	9	Methanol hydrochlorination
Dow Corning, Midland, MI	7	Methanol hydrochlorination
Ethyl, Baton Rouge, LA	46	Methanol hydrochlorination
General Electric, Waterford, NY	23	Methanol hydrochlorination
Stauffer, Louisville, KY	7[b]	Methanol hydrochlorination
Union Carbide, Institute, WV	23	Methanol hydrochlorination
Vulcan, Geismar, LA	c	Methanol hydrochlorination
Vulcan, Wichita, KS	c	Methanol hydrochorination and methane chlorination
Total	283	

[a] See ref 3.

[b] Production ratios vary with amount of methyl chloride separated as product and amount chlorinated for methylene chloride and chloroform manufacture.

[c] All methyl chloride is chlorinated to methylene chloride and chloroform.



1. Allied, Moundsville, WV
2. Continental, Westlake, LA
3. Diamond Shamrock, Belle, WV
4. Dow, Freeport, TX
5. Dow, Palquemine, LA
6. Dow Corning, Carrolton, KY
7. Dow Corning, Midland, MI
8. Ethyl, Baton Rouge, LA
9. General Electric, Waterford, NY
10. Stauffer, Louisville, KY
11. Union Carbide, Institute, WV
12. Vulcan, Geismar, LA
13. Vulcan, Wichita, KS

Fig. II-1. Locations of Plants Manufacturing Methyl Chloride

C. METHYLENE CHLORIDE

1. General Description

Methylene chloride is a heavy, volatile liquid at ambient conditions (see Appendix A for pertinent physical properties) and is produced by chlorination of either methyl chloride or methane. Emissions from its manufacture include all the chloromethanes.

2. Usage and Growth

Table II-3 gives the end uses and expected production growth rates of methylene chloride, which is used predominantly as a solvent. Its nonflammability and low acute toxicity contribute to its popularity as a paint remover.

The current methylene chloride production capacity is about 378,000 Mg/yr,[3] with about 75% of that capacity being utilized in 1979.[4] Based on an estimated 11% annual growth in methylene chloride consumption,[2] the demand will nearly equal the current capacity by 1982.

3. Domestic Producers

In 1979 five domestic producers of methylene chloride were operating seven plants. Table II-4 lists the producers, locations, capacities, and processes being used; Fig. II-2 shows the plant locations. The Dow Chemical plant at Freeport, TX, representing 24% of the total domestic capacity, was the only plant using methane chlorination exclusively for methylene chloride production. The Vulcan plant at Wichita, KS, and the Allied plant have both methane chlorination and methyl chloride chlorination process capabilities. Approximately 5% of Allied's capacity and 10% of Vulcan's capacity are based on the methane chlorination process.[5,6] All other plants use methyl chloride chlorination. All producers manufacture chloromethane co-products, and production ratios vary, depending on the desired end products.

Vulcan's new 63,500-Mg/yr chloromethane plant at Wichita, KS, using the methyl chloride chlorination process, provided additional methylene chloride capacity of 36,300 Mg/yr. Dow reportedly planned to expand its methylene chloride production capacity by late 1979.[3]

Table II-3. Methylene Chloride Usage and Growth[a,b]

End Use	1977 Production (%)
Paint remover	30
Solvent degreasing	20
Plastics process	9
Exports	18
Aerosol	19
Miscellaneous	4

[a] See ref 3.

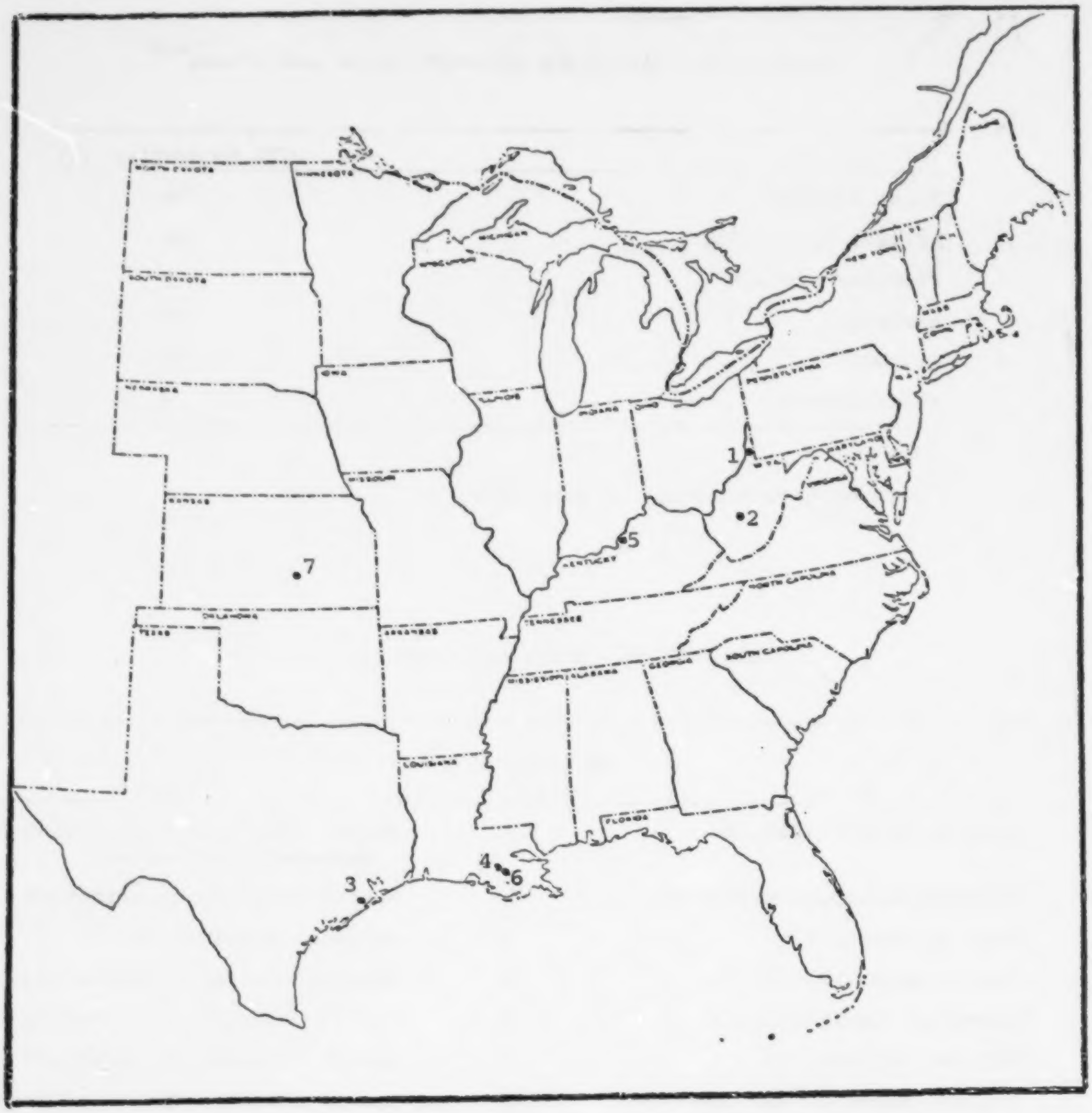
[b] Data on growth rates not available.

Table II-4. Methylene Chloride Capacity[a]

Plant	1977 Capacity[b] (X 10^3 Mg)	Process
Allied, Moundsville, WV	23	Methyl chloride chlorination and methane chlorination
Diamond Shamrock, Belle, WV	50	Methyl chloride chlorination
Dow, Freeport, TX	92	Methane chlorination
Dow, Plaquemine, LA	88	Methyl chloride chlorination
Stauffer, Louisville, KY	28	Methyl chloride chlorination
Vulcan, Geismar, LA	37	Methyl chloride chlorination
Vulcan, Wichita, KS	60	Methyl chloride chlorination and methane chlorination
Total	378	

[a] See ref 3.

[b] Other chloromethanes are manufactured as co-products, and capacities for individual products vary.



1. Allied, Moundsville, WV
2. Diamond Shamrock, Belle, WV
3. Dow, Freeport, TX
4. Dow, Plaquemine, LA
5. Stauffer, Louisville, KY
6. Vulcan, Geismar, LA
7. Vulcan, Wichita, KS

Fig. II-2. Locations of Plants Manufacturing Methylene Chloride

D. CHLOROFORM

1. General Description

Chloroform is a heavy, volatile liquid at ambient conditions (see Appendix A for pertinent physical properties) and is made by chlorination of methyl chloride or methane. Emissions from chloroform manufacture include all the chloromethanes.

2. Usage and Growth

As is shown in Table II-5, the predominant end use of chloroform is as an intermediate in the manufacture of chlorodifluoromethane. Chlorodifluoromethane can be used as a refrigerant, a solvent, or a propellant or in the manufacture of fluororesins, but its main use is as a refrigerant. A ban on fluorocarbon propellants would not significantly affect its production rate.[3]

The current domestic chloroform production capacity is 237,000 Mg/yr,[3] with 1979 production utilizing about 67% of that capacity.[4] Based on an estimated 8% annual growth in chloroform consumption, production would reach 84% of current capacity by 1982.

3. Domestic Producers

In 1979 five domestic producers were operating seven chloroform-producing plants. Table II-6 lists the producers, locations, capacities, and processes being used; Fig. II-3 shows the plant locations. The Dow Chemical plant at Freeport, TX, is the only facility using methane chlorination exclusively for chloroform production. The capacity of this plant is about 20% of the total domestic capacity. The Allied plant, as well as the Vulcan plant at Wichita, KS, has both methane chlorination and methyl chloride chlorination process capabilities. Approximately 5% of Allied's capacity and 10% of Vulcan's capacity are based on methane chlorination.[5,6] All other plants use methyl chloride chlorination exclusively for chloroform production. All producers manufacture chloromethane co-products, and production ratios vary, depending on the desired end products.

Vulcan's new 63,500-Mg/yr chloromethanes plant at Wichita, KS, which was completed in 1977, provided an additional capacity of 27,200 Mg/yr. Dow scheduled an increase in capacity at Freeport, TX, which was to have been brought on-stream late in 1979.[3]

Table II-5. Chloroform Usage[a,b]

	1974 Production (%)
Chlorodifluoromethane	
Refrigerant, solvent, propellant	91
Exports	7
Miscellaneous	2

[a] See ref 3.

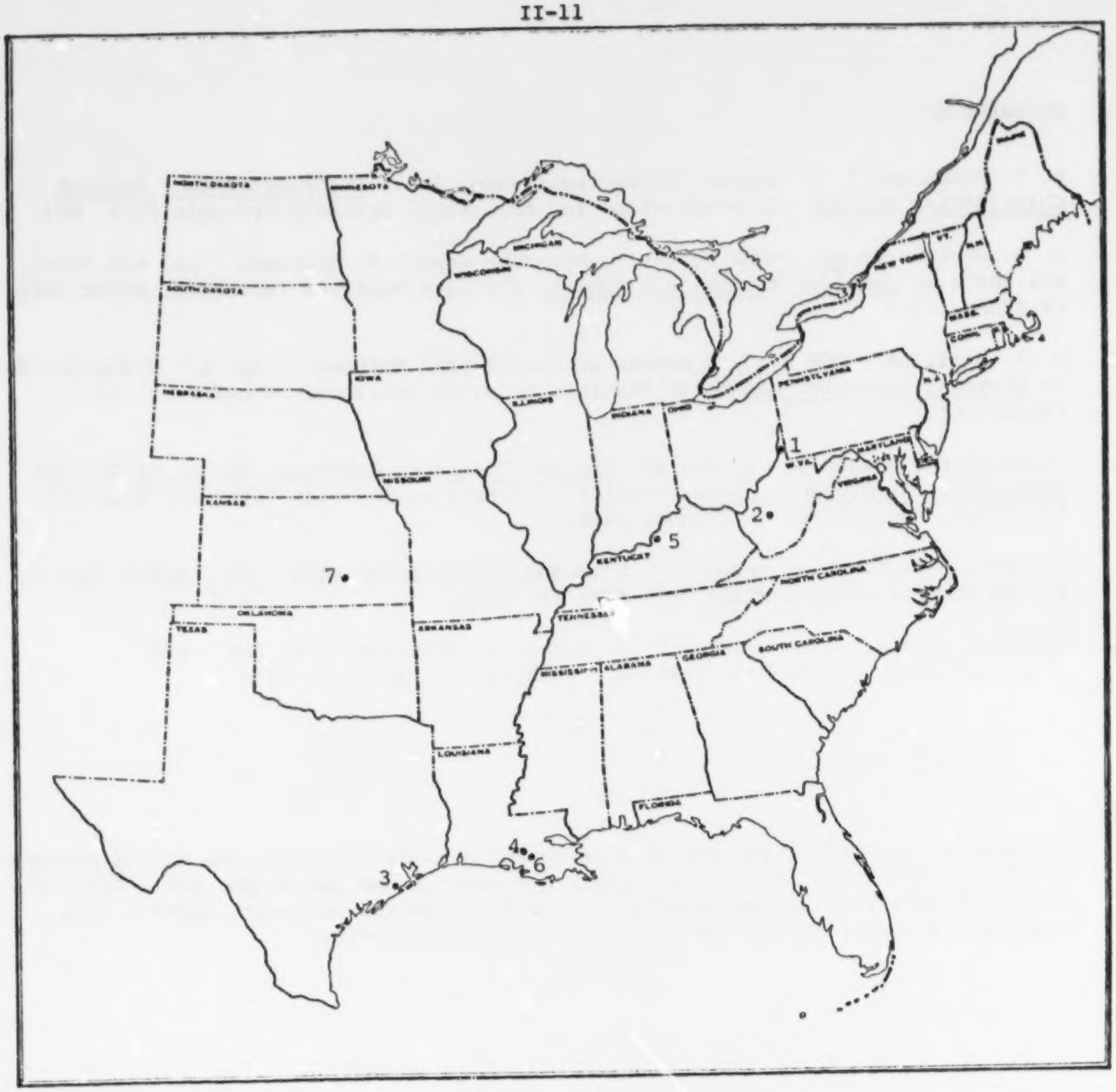
[b] Data on growth rates not available.

Table II-6. Chloroform Capacity[a]

Plant	1979 Capacity[b] (X 10^3 Mg)	Process
Allied, Moundsville, WV	14	Methyl chloride chlorination and methane chlorination
Diamond Shamrock, Belle, WV	18	Methyl chloride chlorination
Dow, Freeport, TX	46	Methane chlorination
Dow, Plaquemine, LA	46	Methyl chloride chlorination
Stauffer, Louisville, KY	34	Methyl chloride chlorination
Vulcan, Geismar, LA	28	Methyl chloride chlorination
Vulcan, Wichita, KS	51	Methyl chloride chlorination and methane chlorination
Total	237	

[a] See ref 3.

[b] Other chloromethanes are manufactured as co-products, and capacities for individual products vary.



NORTH DAKOTA
MINNESOTA
SOUTH DAKOTA
WISCONSIN
MICHIGAN
NEW YORK
VT.
N.H.
MASS.
CONN.
NEBRASKA
IOWA
ILLINOIS
INDIANA
OHIO
PENNSYLVANIA
MARYLAND
W.VA.
VIRGINIA
KANSAS
MISSOURI
KENTUCKY
NORTH CAROLINA
OKLAHOMA
TEXAS
ARKANSAS
TENNESSEE
SOUTH CAROLINA
MISSISSIPPI
ALABAMA
GEORGIA
LOUISIANA
FLORIDA
1
2
3
4
5
6
7

1. Allied, Moundsville, WV
2. Diamond Shamrock, Belle, Wv
3. Dow, Freeport, TX
4. Dow, Plaquemine, LA
5. Stauffer, Louisville, KY
6. Vulcan, Geismar, LA
7. Vulcan, Wichita, KS

Fig. II-3. Locations of Plants Manufacturing Chloroform

E. REFERENCES*

1. F. D. Hobbs and C. W. Stuewe, IT Enviroscience, Inc., Chloromethanes. Methane Chlorination Process (in preparation for EPA, ESED, Research Triangle Park, NC).

2. A. D. Obshire *et al*., "CEH Marketing Research Report on Methanol," pp. 674.5023I-674.5033S in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (June 1980).

3. T. F. Killilea, "CEH Product Review on Chlorinated Methanes," pp. 625.2030A-635.2031G in Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (April 1979).

4. "Chlorinated Methanes," p. 244 in Chemical Economics Handbook, Manual of Current Indicators--Supplemental Data, Chemical Information Services, Stanford Research Institute, Menlo Park, CA (August 1980).

5. Personal communication between F. D. Hobbs, IT Enviroscience, Inc., and D. Denoon, Allied Chemical, Moundsville, WV, July 25, 1978.

6. Personal communication between F. D. Hobbs, IT Enviroscience, Inc., and T. A. Robinson, Vulcan Materials Co., Wichita, KS, July 28, 1978.

*A reference located at the end of a paragraph usually refers to the entire paragraph. If another reference relates to certain portions of the paragraph, the reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

III. PROCESS DESCRIPTION

A. INTRODUCTION

In the United States the main processes of producing chloromethanes consist of methanol hydrochlorination followed by further chlorination of the methyl chloride produced.[1] In 1979 about 89% of methyl chloride, 70% of methylene chloride, and 75% of chloroform capacities in the United States were based on these processes. Some carbon tetrachloride is formed as a by-product in the chlorination of methyl chloride but is not generally directly purified into product by domestic producers. The unpurified carbon tetrachloride is either sold as is or is used in-house as feed to carbon tetrachloride--perchloroethylene producing facilities.

B. METHANOL HYDROCHLORINATION AND METHYL CHLORIDE CHLORINATION PROCESSES

1. Basic Process

Although some domestic producers manufacture methyl chloride exclusively by hydrochlorination of methanol, it is common practice to combine this reaction with the continuous chlorination of methyl chloride to produce methylene chloride and chloroform, along with carbon tetrachloride in small amounts as a by-product. These two processes are discussed as an integral process for the purpose of this report.

Methyl chloride is produced by the reaction

$$\underset{\text{(Methanol)}}{CH_3OH} + \underset{\text{(Hydrogen Chloride)}}{HCl} \longrightarrow \underset{\text{(Methyl Chloride)}}{CH_3Cl} + \underset{\text{(Water)}}{H_2O}$$

Methylene chloride, chloroform, and by-product carbon tetrachloride are then produced from methyl chloride by the reactions

$$\underset{\text{(Methyl Chloride)}}{CH_3Cl} + \underset{\text{(Chlorine)}}{Cl_2} \longrightarrow \underset{\text{(Methylene Chloride)}}{CH_2Cl_2} + \underset{\text{(Hydrogen Chloride)}}{HCl}$$

$$\underset{\text{(Methylene Chloride)}}{CH_2Cl_2} + \underset{\text{(Chlorine)}}{Cl_2} \longrightarrow \underset{\text{(Chloroform)}}{CHCl_3} + \underset{\text{(Hydrogen Chloride)}}{HCl}$$

$$\underset{\text{(Chloroform)}}{CHCl_3} + \underset{\text{(Chlorine)}}{Cl_2} \longrightarrow \underset{\text{(Carbon Tetrachloride)}}{CCl_4} + \underset{\text{(Hydrogen Chloride)}}{HCl}$$

A typical continuous-process flow diagram for the basic process is shown in Fig. III-1.

Methanol is hydrochlorinated by feeding equimolar proportions of vaporized methanol (Stream 1) and hydrogen chloride (Stream 2) at 180--200°C to the hydrochlorination reactor. The reactor is packed with any one of a number of catalysts, including alumina gel, cuprous or zinc chloride on activated carbon or pumice, or phosphoric acid on activated carbon. The reactor is maintaned at a temperature of about 350°C. The reaction is exothermic. Methanol conversion of 95% is typical.[1]

The reactor exit gases (Stream 3) enter the quench tower, where unreacted hydrogen chloride and methanol are removed by water scrubbing. The discharge from the quench tower (Stream 4) is stripped of virtually all dissolved methyl chloride and most of the methanol, both of which are recycled to the hydrochlorination reactor (Stream 5). The remaining aqueous solution from the stripper (Stream 6) consists of dilute hydrochloric acid, which is used in-house or is sent to wastewater treatment.[2]

Methyl chloride from the quench tower (Stream 7) is fed to the drying tower, where concentrated sulfuric acid removes residual water. The dilute sulfuric acid effluent (Stream 8) is sold or is reprocessed.[2]

A portion of the dried methyl chloride (Stream 9) is compressed, cooled, and liquefied as product. The rest of the dried methyl chloride (Stream 10) is fed to the chlorination reactor. The methyl chloride and chlorine (Stream 11) are mixed in the reaction chamber to form methylene chloride and chloroform, along with hydrogen chloride and a small amount of carbon tetrachloride. The reactions are exothermic.

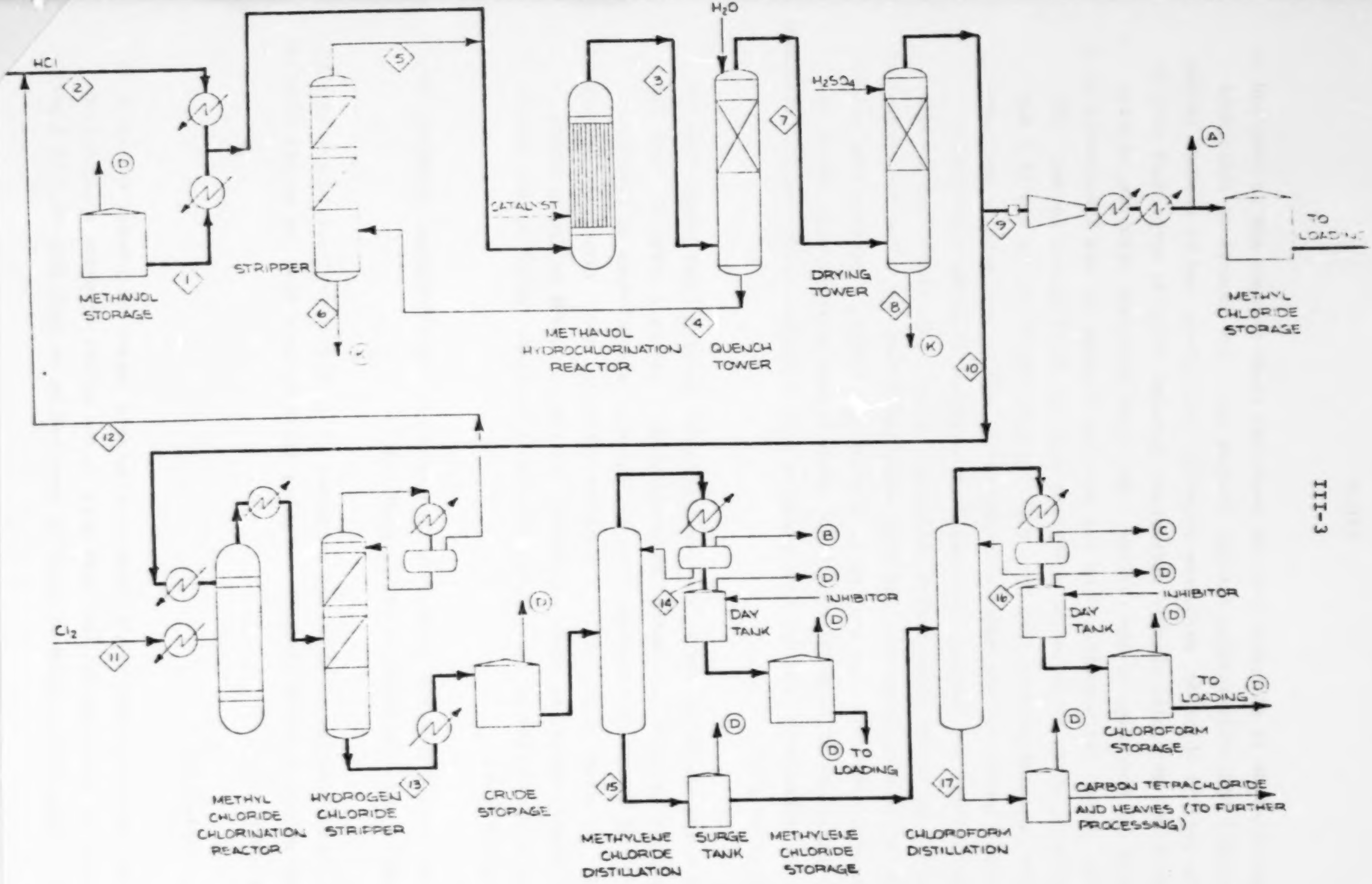

HCl
2
METHANOL STORAGE
D
1
STRIPPER
6
K
5
CATALYST
METHANOL HYDROCHLORINATION REACTOR
3
H$_2$O
QUENCH TOWER
4
7
H$_2$SO$_4$
DRYING TOWER
8
K
9
10
A
METHYL CHLORIDE STORAGE
TO LOADING
12
Cl$_2$
11
METHYL CHLORIDE CHLORINATION REACTOR
HYDROGEN CHLORIDE STRIPPER
13
CRUDE STORAGE
D
METHYLENE CHLORIDE DISTILLATION
15
14
B
D
INHIBITOR
DAY TANK
D
SURGE TANK
D
METHYLENE CHLORIDE STORAGE
D TO LOADING
CHLOROFORM DISTILLATION
17
16
C
D
INHIBITOR
DAY TANK
D
CHLOROFORM STORAGE
TO LOADING
D
D
CARBON TETRACHLORIDE AND HEAVIES (TO FURTHER PROCESSING)

Fig. III-1. Process Flow Diagram for Manufacture of Chloromethanes by Methanol Hydrochlorination and Methyl Chloride Chlorination Processes

Hydrogen chloride is stripped from the condensed crude product and is recycled to the methanol hydrochlorination reactor (Stream 12). The amounts of individual products (methyl chloride, methylene chloride, chloroform, and by-product carbon tetrachloride) determine whether sufficient hydrogen chloride by-product will be available for operation of the reactor. The crude methylene chloride, chloroform, and carbon tetrachloride from the stripper (Stream 13) are transferred to a storage tank, which feeds to the methylene chloride distillation column. The methylene chloride product from this distillation (Stream 14) is fed to a day tank, where inhibitors are added as stabilizers, and is then sent to methylene chloride storage and loading. Bottoms from methylene chloride distillation (Stream 15) go to the chloroform distillation column. The chloroform product (Stream 16) is also taken to a day tank where inhibitors are added for control of hydrochloric acid, and then sent on to storage and loading. Bottoms from chloroform distillation (Stream 17) consist of crude carbon tetrachloride, which is stored for subsequent transfer to a separate carbon tetrachloride--perchloroethylene process or is sold.

Process emissions originate at the vents used for purging inert gases from the condensers associated with methyl chloride product recovery (Vent A), with distillation of methylene chloride (Vent B), and with distillation of chloroform (Vent C), as shown in Fig. III-1. Fugitive emissions occur when leaks develop in valves, pumps, seals, or other equipment. Corrosion caused by the hydrogen chloride and chlorine in the process can result in leaks, which hinder control of fugitive emissions.

Emissions result from the storage of feed material, intermediates, products, and by-products and from handling of the products.

Two potential sources of secondary emissions (K on Fig. III-1) are aqueous wastes from the methyl chloride stripper and waste sulfuric acid from the methyl chloride drying tower.

2. Process Variations

a. A process variation that would cause considerable impact on process emissions is the purity of the chlorine feed that goes to the methyl chloride chlorination reactor. Commercial liquid chlorine is reported to be typically 99.6 wt % pure, although amounts of impurities vary considerably.[3] The model plant was based on a 99.6 wt % pure chlorine feed, which can be achieved by liquefying and revaporizing the chlorine before it is used. Without this purification step there will be additional inert gases, including carbon dioxide, oxygen, and hydrogen, in the chlorine,[4] which will increase emissions from the inert-gas purge vent (Vent A, Fig. III-1).

b. Another process variation is the use of all methyl chloride produced in the manufacture of methylene chloride and chloroform. Inert gases introduced with the chlorine must still be removed from the system.

c. An additional variation consists of the hydrochlorination reaction being carried out in the liquid phase by refluxing the methanol at 150°C with hydrochloric acid in the presence of dissolved zinc chloride.[1] This change would have an insignificant effect on overall process emissions.

d. Variation of reaction conditions in the methyl chloride chlorination reactor changes co-product and by-product yield ratios and therefore changes the relative amounts of storage and loading emissions from each product stream.

e. When caustic scrubbing is used to remove residual hydrogen chloride from methyl chloride before it is dried and from the crude product exiting the hydrogen chloride stripper, chloromethanes will be carried from the process in the waste caustic and will be emitted during treatment or disposal of the waste. Also, drying columns are used for removing trace amounts of water from the methylene chloride and chloroform product streams following distillation, thereby creating other sources of secondary emissions.

f. Nitrogen is reported to be used for safety purposes during loading and unloading of methyl chloride. This practice creates a source of methyl chloride emissions.[5]

g. Methane is used by one producer to maintain proper process pressure. Also, the same producer uses tail gas chlorine from a caustic-chlorine plant to feed the chlorination reactor.[6]

C. REFERENCES

1. D. W. F. Hardie, "Chlorocarbons and Chlorohydrocarbons," pp. 105, 106 in Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 5, 2d ed., Interscience, New York, 1964.

2. F. D. Hobbs, IT Enviroscience, Inc., Trip Report for Visit to Vulcan Materials Company, Geismar, LA, Jan. 4, 1978 (data on file at EPA, ESED, Research Triangle Park, NC).

3. "Purity of Commercial Chlorine," Sect. 1, p. 2 in Hooker Chlorine, Bulletin No. 125, Hooker Chemical Corp. (1965).

4. T. A. Liederbach, "Reducing Chlorine Loss in an Electrolysis Plant," Chemical Engineering Progress **70**(3), 64--68 (1974).

5. S. G. Lant, Diamond Shamrock, Belle, WV, letter to D. R. Goodwin, EPA, Apr. 3, 1978.

6. Personal communication between F. D. Hobbs, IT Enviroscience, Inc., and D. Denson, Allied Chemical, Moundsville, WV, July 25, 1978, and Sept. 14, 1978.

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*A reference located at the end of a paragraph usually refers to the entire paragraph. If another reference relates to certain portions of the paragraph, the reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

IV. EMISSIONS FOR MODEL PLANTS

Emissions in this report are usually identified in terms of volatile organic compounds (VOC). VOC are currently considered by the EPA to be those of a large group of organic chemicals, most of which, when emitted to the atmosphere participate in photochemical reactions producing ozone. A relatively small number of organic chemicals have low or negligible photochemical reactivity. However, many of these organic chemicals are of concern and may be subject to regulation by EPA under Sections 111 and 112 of the Clean Air Act since there are associated health or welfare impacts other than those related to ozone formation. It should be noted that although methylene chloride is included in VOC emission totals in this report, it does not, based on current research data, participate in ozone-forming reactions to an appreciable extent.

A. METHANOL HYDROCHLORINATION AND METHYL CHLORIDE CHLORINATION

1. Model Plants*

Three model plants, with chloromethane capacities of 45,000, 90,000, and 180,000 Mg/yr, were selected to represent current domestic chloromethane manufacturing facilities. The percentages of total capacity for individual products were selected to be 25% methyl chloride, 48% methylene chloride, 25% chloroform, and 2% by-product carbon tetrachloride. For these percentages of the products there is insufficient hydrogen chloride by-product from the methyl chloride chlorination reaction for the methanol hydrochlorination reaction. Typical raw-material, intermediate, and product storages were selected according to these percentages of individual products. Each model plant was assumed to operate 8760 hr annually.**

The model methanol hydrochlorination and methyl chloride chlorination processes shown in Fig. III-1 reflect today's manufacturing and engineering technology.

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*See page I-2 for a discussion of model plants.

**Process downtime is normally expected to range from 5 to 15%. If the hourly rate remains constant, the annual production and annual VOC emissions will be correspondingly reduced. Control devices will usually operate on the same cycle as the process. From the standpoint of cost-effectiveness calculations, the error introduced by assuming continuous operation is negligible.

Single process trains are typical. The number of valves, pumps, and compressors used for calculating fugitive emissions is typical for a plant of this type. Characteristics of the model plants important to air dispersion are shown in Appendix B.

2. Sources and Emissions

The process emissions estimated for the methanol hydrochlorination and methyl chloride chlorination processes described in this report and shown in Table IV-1 are based on the emissions reported in response to EPA's requests for information, on a trip report on a visit to Vulcan, on a permit filed with the State of Texas by Diamond Shamrock for a proposed chloromethanes plant, and on an understanding of the process chemistry and yields.

b. Process Emissions -- Process emissions originate at the inert-gas purge vent and at the methylene chloride and chloroform condensers, as described below:

Inert-gas purge vent -- The chlorine feed to the methyl chloride chlorination reactor contains inert gases, which must be vented. The model plants are based on a chlorine feed that is purified (liquefied and revaporized) and is 99.6 wt % pure. The inert gases will flow with the hydrogen chloride (Stream 12, Fig. III-1) recycled to the hydrochlorination reactor from the hydrogen chloride stripper following the methyl chloride chlorination reactor. These gases will remain in the closed system until vented (Vent A, Fig. III-1), after compression and condensation of the methyl chloride.

Calculations based on 99.6 wt % pure chlorine for methyl chloride chlorination, compression to a pressure of 5.07×10^5 Pa, and brine condensation of methyl chloride at -20°C indicate emissions of 1.5×10^{-3} kg of methyl chloride per kg of total chloromethanes produced. Variations in chlorine purity will significantly affect emissions. For example, calculations based on 99.2 wt % pure chlorine, with other conditions remaining identical, would double the methyl chloride emissions, to 3.0 kg $\times 10^{-3}$, per kg of total chloromethanes produced. Use of tail-gas chlorine would significantly increase the potential for emissions. Sample calculations for determining the emissions indicated in Table IV-1 are shown in Appendix C.

Table IV-1. Total Uncontrolled[a] VOC Emissions for Model Plants Producing Chloromethanes by Methanol Hydrochlorination and Methyl Chloride Chlorination

Source	Stream Designation (Fig. III-1)	Total VOC Emissions[b] for Model Plants					
		45,000-Mg/yr Model Plant		90,000-Mg/yr Model Plant		180,000-Mg/yr Model Plant	
		Ratio[c] (kg/Mg)	Rate (kg/hr)	Ratio[c] (kg/Mg)	Rate (kg/hr)	Ratio[c] (kg/Mg)	Rate (kg/hr)
Inert-gas purge vent	A	1.5	7.85	1.5	15.7	1.5	31.4
Methylene chloride condenser[d]	B	0.019	0.10	0.019	0.20	0.019	0.39
Chloroform condenser[d]	C	0.0056	0.029	0.0056	0.058	0.0056	0.12
In-process storage[e]	D	0.55	2.80	0.54	5.56	0.53	10.83
Feed and product storage[e]	D	1.07	5.48	1.03	10.55	1.02	20.92
By-product storage[e,f]	D	0.03	0.14	0.03	0.31	0.03	0.59
Handling[e]	D	0.36	1.84	0.36	3.68	0.36	7.36
Fugitive	F	2.9	14.9	1.45	14.9	0.73	14.9
Secondary	K	0.020	0.10	0.020	0.21	0.020	0.41
		6.45	33.2	4.93	51.1	4.21	86.9

[a] Uncontrolled emissions are emissions from processes using no additional control devices other than those necessary for economical operation.

[b] Emissions include methyl chloride, methylene chloride, chloroform, carbon tetrachloride, dimethyl ether, and methanol.

[c] kg of emissions per Mg of chloromethane produced.

[d] See ref. 1.

[e] See ref. 2.

[f] Carbon tetrachloride plus "heavies" (or heavy ends).

Methylene chloride and chloroform condensers -- Two sources of process emissions result from the buildup of inert gases in the condensers associated with methylene chloride and chloroform distillation (Vents B and C, Fig. III-1) These gases must occasionally be purged to ensure efficient condenser performance. Emissions are reported to be 1.9 X 10^{-5} kg of methylene chloride per kg of total chloromethanes produced for vent B and 5.6 X 10^{-6} kg of chloroform per kg of total chloromethanes produced for vent C. The temperature of the vented materials was reported to be 43°C for both vents.[1]

c. Fugitive Emissions -- Process pumps, valves, and compressors are potential sources of fugitive emissions. Each model plant is estimated to have 30 pumps handling VOC (includes 15 spares), 750 process valves, including 25 pressure-relief valves, and 2 compressors. All pumps have mechanical seals. The factors shown in Appendix D were used to determine the fugitive emissions listed in Table IV-1.

d. Storage and Handling Emissions -- Emissions result from storage and handling of methanol, methylene chloride, chloroform, and by-product crude carbon tetrachloride. Because methyl chloride has to be stored in pressure vessels, no methyl chloride losses are involved except for emissions that would be classified as fugitive emissions. The sources of storage emissions for the model plants are shown on the flow diagram in Fig. III-1 (Source D). Storage tank conditions for the model plants are given in Table IV-2. The uncontrolled storage emissions in Table IV-1 were calculated with the emission equations from AP-42,[2] with the tanks assumed to have fixed roofs and on the average to be half full, with a diurnal temperature variation of 12°C. However, breathing losses were divided by 4 to account for recent evidence indicating that the AP-42 breathing loss equation overestimates emissions.[3]

Emissions from loading methylene chloride and chloroform product into tank cars and trucks were calculated with the equations from AP-42.[2] Submerged loading into clean tank cars and trucks was assumed for the emission calculations. No emissions from loading carbon tetrachloride are included for the model plant, since it is assumed that this impure by-product is transferred for further processing in a carbon tetrachloride--perchloroethylene co-product facility. Another assumption was that methyl chloride loading has a vapor return loop and therefore creates no emissions.

Table IV-2. Storage Requirements for Model Plants Producing Chloromethanes by Methanol Hydrochlorination and Methyl Chloride Chlorination

Material Stored	Storage Requirements for Model Plants								
	45,000-Mg/yr Model Plant			90,000-Mg/yr Model Plant			180,000-Mg /yr Model Plant		
	Tank Size (m^3)	Turnovers Per Year	Bulk Liquid Temperature (°C)	Tank Size (m^3)	Turnovers Per Year	Bulk Liquid Temperature (°C)	Tank Size (m^3)	Turnovers Per Year	Bulk Liquid Temperature (°C)
Methanol	946	24	20	1890	24	20	3780	24	20
Methyl chloride (2 identical pressure-vessel tanks)	473	13	20	946	13	20	1890	13	20
Methylene chloride--chloroform--carbon tetrachloride[a]	95	6[b]	35	189	6[b]	35	378	6[b]	35
Methylene chloride (2 identical tanks)	38	216	30	76	216	30	151	216	30
Methylene chloride	946	17	20	1890	17	20	3780	17	20
Chloroform--carbon tetrachloride[a]	38	6[b]	40	76	6[b]	40	151	6[b]	40
Chloroform (2 identical tanks)	19	199	40	38	199	40	76	199	40
Chloroform	378	20	20	758	20	20	1510	20	20
Carbon tetrachloride[a]	19	32	40	38	32	40	76	32	40

[a] Carbon tetrachloride plus "heavies."

[b] Surge tanks are normally operated at constant level.

e. Secondary Emissions -- Secondary VOC emissions can result from the handling and disposal of process waste liquid. For the model plants two potential sources of secondary emissions from waste liquid are indicated on the flow diagram (Source K, Fig. III-1): the aqueous waste discharge from the methanol hydrochlorination process stripper and the sulfuric acid waste from the methyl chloride drying tower.

Aqueous waste discharged from a properly designed and operated stripper, which removes methanol and methyl chloride from the quench tower discharges for recycle to the methanol hydrochlorination reactor, will contain some residual methanol, but this methanol is not considered to be a source of secondary emissions because it has a high solubility and a low volatility and is biodegradable.

Waste sulfuric acid from the methyl chloride drying tower is reported to contain dimethyl ether, a by-product of the methanol hydrochlorination reaction.[4—6] Based on the reported data[4—6] the waste acid is estimated to contain 4.2 X 10^{-3} kg of dimethyl ether per kg of total chloromethane capacity, along with lesser quantities of methanol and methyl chloride. One producer reported[4] the waste acid to contain 2 wt % dimethyl ether, 0.3 wt % methanol, and 0.1 wt % methyl chloride. Based on these relative amounts of individual VOC components and the estimated 4.2 X 10^{-3} kg of dimethyl ether per kg of total chloromethane capacity, the waste acid is calculated to contain 6.3 X 10^{-4} kg methanol and 2.1 X 10^{-4} kg of methyl chloride in addition to the dimethyl ether, for a total VOC content of about 5.0 X 10^{-3} kg per kg of total chloromethane capacity. One producer reported that a nitrogen purge on the waste acid tank results in emissions of 4.9 X 10^{-2} kg/hr, or about 1.9 X 10^{-5} kg of dimethyl ether combined with sulfuric acid per kg of capacity, and unspecified but lesser quantities of free dimethyl ether and methyl chloride.[7] Another producer reported that the VOC in the waste acid is not considered to be volatile and is oxidized during the acid recovery process.[5] Consequently, based on the above information, the model plant is estimated to have 2.0 X 10^{-5} kg of secondary VOC emissions from the waste acid per kg of total chloromethane capacity, with the remaining VOC oxidized during waste acid recovery. It can be be noted that there are wide variations in the reported amounts of VOC in the waste acid, the major source of estimated secondary VOC emissions.

B. OTHER PROCESSES

The methane chlorination and mixed hydrocarbon chlorinolysis processes to produce chloromethanes will be covered in future reports. The only other process of significance is the chlorination of carbon disulfide to produce carbon tetrachloride. Because of the negative growth of the carbon tetrachloride market this process is becoming less important.

C. REFERENCES*

1. F. D. Hobbs, IT Enviroscience, Inc., Trip Report for Vulcan Materials Company, Geismar, LA, Jan. 4, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

2. C. C. Masser, "Storage of Petroleum Liquids," pp. 4.3-1 to 4.3-11 in Supplement No. 7 for Compilation of Air Pollutant Emission Factors, AP-42, 2d ed., EPA, Research Triangle Park, NC (April 1977).

3. E. C. Pulaski, TRW, letter dated May 30, 1979, to Richard Burr (EPA).

4. J. V. Muthig, Allied Chemical, Moundsville, WV, letter to D. R. Goodwin, EPA, Mar. 31, 1978.

5. W. C. Strader, Ethyl Corporation, Baton Rouge, LA, letter to D. R. Goodwin, EPA, Aug. 2, 1978.

6. Personal communication between D. A. Beck, EPA, Research Triangle Park, NC, and J. Romans, Dow Corning, Carrolton, KY, Sept. 1, 1978.

7. R. L. Hatch, General Electric, Waterford, NY, letter to D. R. Goodwin, EPA, Aug. 8, 1978.

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*A reference located at the end of a paragraph usually refers to the entire paragraph. If another reference relates to certain portions of the paragraph, the reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

V. APPLICABLE CONTROL SYSTEMS

A. EMISSION CONTROLS FOR MODEL PLANTS

1. Process Emissions

a. Inert-Gas Purge Vent -- The absorption unit operation is a common concept for the recovery of light hydrocarbons by their absorption in less volatile oils. A similar operation conceptually can be used for absorption of methyl chloride in chloroform for producers who manufacture the higher chloromethanes from methyl chloride. Chloroform could be drawn from the process, chilled, and used as the absorbent. The amount of VOC controlled would be dependent on the operating temperature and pressure of the absorber. An operating temperature of -40°C would result in a net control of VOC of about 98.8% at the design pressure of 5.1×10^5 Pa.

A preliminary design was developed of an adsorber system for cost estimating purposes per the standard design methods described by Treybal.[1] The design was not optimized. The large difference in volatility between methyl chloride and chloroform and the relatively small column size make the absorption column height, within practical engineering limits, unimportant for either control efficiency or system cost. The design parameters with the greatest effect on the control efficiency are final gas temperature and pressure. As a general relationship the total VOC emitted from the absorber will vary directly with the absolute pressure of the system. Therefore the efficiency of 98.8% achievable at design pressure and temperature will decrease to about 94% with a decrease to atmospheric pressure.

The absorber system may not be practical for use at existing plants. The limitations on existing chloroform distillation capacity might disallow the use of this control device without prohibitive equipment modifications. Further information is listed in Appendix E, "Current Industry Considerations."

Carbon adsorption is not considered to be a practical alternative. Methyl chloride has a very low loading factor on carbon due to its high volatility at practical temperatures and pressures. Additionally, the feed stream is too concentrated in methyl chloride to be fed to a carbon column; therefore the feed stream would have to be diluted with additional inert gases. Both factors would contribute to a high cost per unit of methyl chloride removed.

Thermal oxidation also was not considered a sufficiently viable option to justify a comparative study. Formation of hydrogen chloride during oxidation of methyl chloride would necessitate corrosion-resistant materials of construction and the addition of a scrubber for the vent gases from the oxidizer. Both would contribute to high capital and operating costs.

Controlled inert-gas purge-vent emissions for the 45,000- 90,000-, and 180,000-Mg/yr model plants are given in Table V-1.

b. Methylene Chloride and Chloroform Condensers -- Losses of VOC from the methylene chloride and chloroform distillation vents (Vents B and C, Fig. III-1) constitute less than 1% of emissions from the model plants. For the model plants these two sources remain uncontrolled.

2. Fugitive Emissions

Control for fugitive sources is discussed in a separate EPA report.[2] The controlled fugitive emissions shown in Table V-1 are based on the factors given in Appendix D and on the assumption that any major leaks would be detected and repaired.

3. Storage Emissions

Condensation is used to control emissions from storage of chloromethanes. The use of condensation is assumed to provide 80% control for model-plant storage except for by-product storage, which is assumed to remain uncontrolled. Total SOCMI VOC storage emissions are covered by a separate EPA report.[3]

4. Handling Emissions

No unique handling controls are known to be practiced by the industry. Therefore the handling emissions for the controlled model plants are the same as those for the uncontrolled plants.

Table V-1. Controlled VOC Emissions[a] for 45,000-, 90,000-, and 180,000-Mg/yr Model Plants Producing Chloromethanes by Methanol Hydrochlorination and Methyl Chloride Chlorination

Source	Steam Designation (Fig. III-1)	Control Device or Technique	VOC Emissions								
			45,000-Mg/yr Model Plant			90,000-Mg/yr Model Plant			180,000-Mg/yr Model Plant		
			Reduction (%)	Ratio[b] (kg/Mg)	Rate (kg/hr)	Reduction (%)	Ratio[b] (kg/mg)	Rate (kg/hr)	Reduction (%)	Ratio[b] (kg/Mg)	Rate (kg/hr)
Inert-gas purge vent	A	Absorber	98.8	0.019	0.10	98.8	0.019	0.20	98.8	0.019	0.40
Methylene chloride condenser	B	None		0.019	0.10		0.019	0.20		0.019	0.39
Chloroform condenser	C	None		0.0056	0.029		0.0056	0.058		0.0056	0.12
In-process storage Feed and product storage	D D	Condenser	80.0	0.32	1.66	80.0	0.31	3.22	80.0	0.31	6.35
By-product storage[c]	D	None		0.038	0.20		0.048	0.49		0.042	0.86
Handling	D	None		0.36	1.84		0.36	3.68		0.36	7.36
Fugitive	F	Detection and repair of leaks	67.5	0.94	4.84	67.5	0.47	4.84	67.5	0.24	4.84
Secondary	K	None		0.020	0.10		0.020	0.21		0.020	0.41
Total				1.72	8.87		1.25	12.9		1.02	20.7

[a] Emissions include methyl chloride, methylene chloride, chloroform, carbon tetrachloride, dimethyl ether, and methanol.

[b] kg of emissions per Mg of chloromethane produced.

[c] Carbon tetrachloride plus "heavies".

5. Secondary Emissions

Secondary emissions originating from the waste sulfuric acid from the methyl chloride drying tower are less than 1% of emissions from the model plants and therefore are not controlled. Emissions from secondary sources are discussed in a separate EPA report.[4]

B. REFERENCES[*]

1. R. E. Treybal, Mass-Transfer Operations, chaps. 6 and 8, McGraw-Hill, New York, 1955.

2. D. G. Erikson and V. Kalcevic, IT Enviroscience, Inc., Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

3. D. G. Erikson, IT Enviroscience, Inc., Storage and Handling (September 1980) (EPA/ESED report, Research Triangle Park, NC).

4. J. Cudahy and R. L. Standifer, IT Enviroscience, Inc., Secondary Emissions (June 1980) (EPA/ESED report, Research Triangle Park, NC).

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[*] A reference located at the end of a paragraph usually refers to the entire paragraph. If another reference relates to certain portions of the paragraph, the reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

VI. IMPACT ANALYSIS

A. CONTROL COST IMPACT

This section presents estimated costs and cost-effectiveness data for control of VOC emissions resulting from the production of chloromethanes. Details of the model plants are given in Sect. III. Emission sources and emissions are discussed in Sect. IV.

Capital cost estimates represent the total investment required for the purchase and installation of all new equipment needed for a complete emission control system performing as defined for a typical location. These estimates do not include the cost of production lost during installation of control systems or the cost of research and development.

The bases for annual cost estimates for the control devices include utilities, raw materials, maintenance supplies and labor, recovery credits, capital charges, and miscellaneous recurring costs such as taxes, insurance, and administrative overhead. (Manpower costs are minimal and therefore are not included.) The cost factors that were used are itemized in Table VI-1. Recovery credits are based on raw-material values. Annual costs are for a 1-year period beginning December 1979.

1. Process Emissions

The major process emission source is the inert-gas purge vent (Vent A, Fig. III-1). The estimated installed capital costs of an absorption system for controlling emissions from this vent are $65,700, $82,400, and $118,600 for the 45,000-, 90,000-, and 180,000-Mg/yr total capacity model plants, respectively (see Table VI-2). Utilities, raw materials, fixed costs, and recovery credits vary with the plant capacity. Installed capital cost, net annual cost, and cost-effectiveness variations with capacity are shown in Figs. VI-1 to VI-3. The absorbent material for methyl chloride in the emissions is chloroform from the process. Annual absorbent material costs are based on the raw-material value of the chloroform (methyl chloride and chlorine) lost from the absorption system. Recovery credits are based on the raw-material value of the methyl chloride (methanol and hydrogen chloride), which is recycled to the process.

Table VI-1. Cost Factors Used in Computing Annual Costs

Item	Factor
Utilities	
Electricity	$8.33/GJ
Cooling water	$0.026/m^3
Operating time	8,760 hr/yr
Operating labor	Minor; not considered
Fixed costs	
Maintenance labor plus materials, 6%	29% of installed cost
Capital recovery, 18% (10 yr life @ 12% interest)	
Taxes insurance, administration, 5%	
Recovery credits*	
Methyl chloride	$337/Mg
Chloroform	$344/Mg

*Based on raw-material costs in "Current Prices of Chemicals and Related Materials," Chemical Marketing Reporter, April 1, 1980.

Table VI-2. Absorber System Control Cost Summary

	Model Plant		
	45,000 Mg/yr	90,000 Mg/yr	180,000 Mg/yr
December 1979 installed capital	$65,700	$82,400	$118,600
Utilities	956	1,854	3,707
Raw materials* (chloroform loss)	226	452	904
Fixed costs	19,053	23,896	34,394
Recovery credits* (methyl chloride recovery)	(23,056)	(46,112)	(92,224)
Net annualized cost (savings)	(2,821)	(19,910)	(53,219)
Total VOC reduction	68 Mg	13 Mg	272 Mg
Cost effectiveness (savings/Mg)	($41/Mg)	($146/Mg)	($195/Mg)

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[*] Based on raw-material costs.

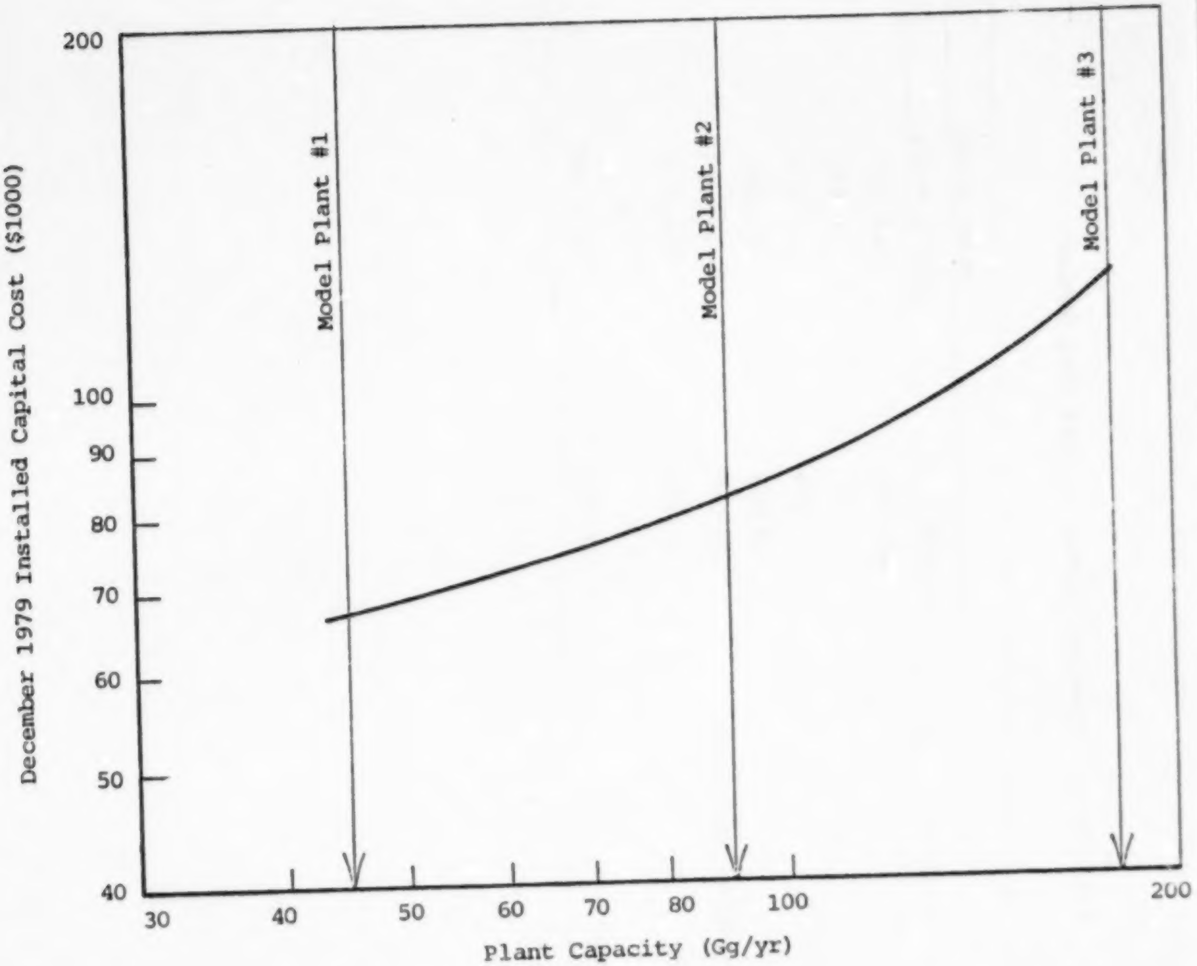

Fig. VI-1. Installed Capital Cost vs Plant Capacity for Inert-Gas Purge Vent Emission Control

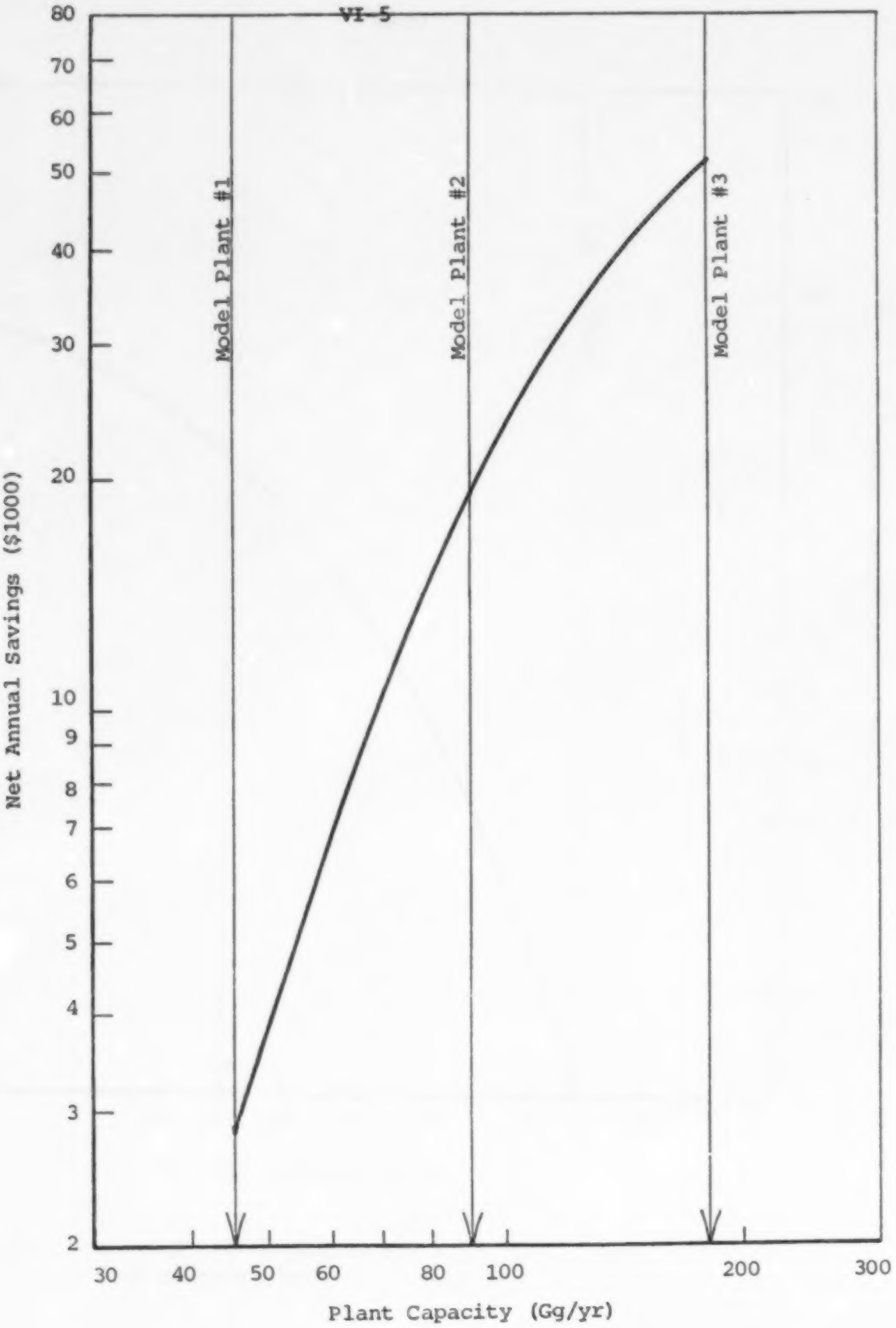

Fig. VI-2. Net Annual Savings vs Plant Capacity for Inert-Gas Purge Vent Emission Control

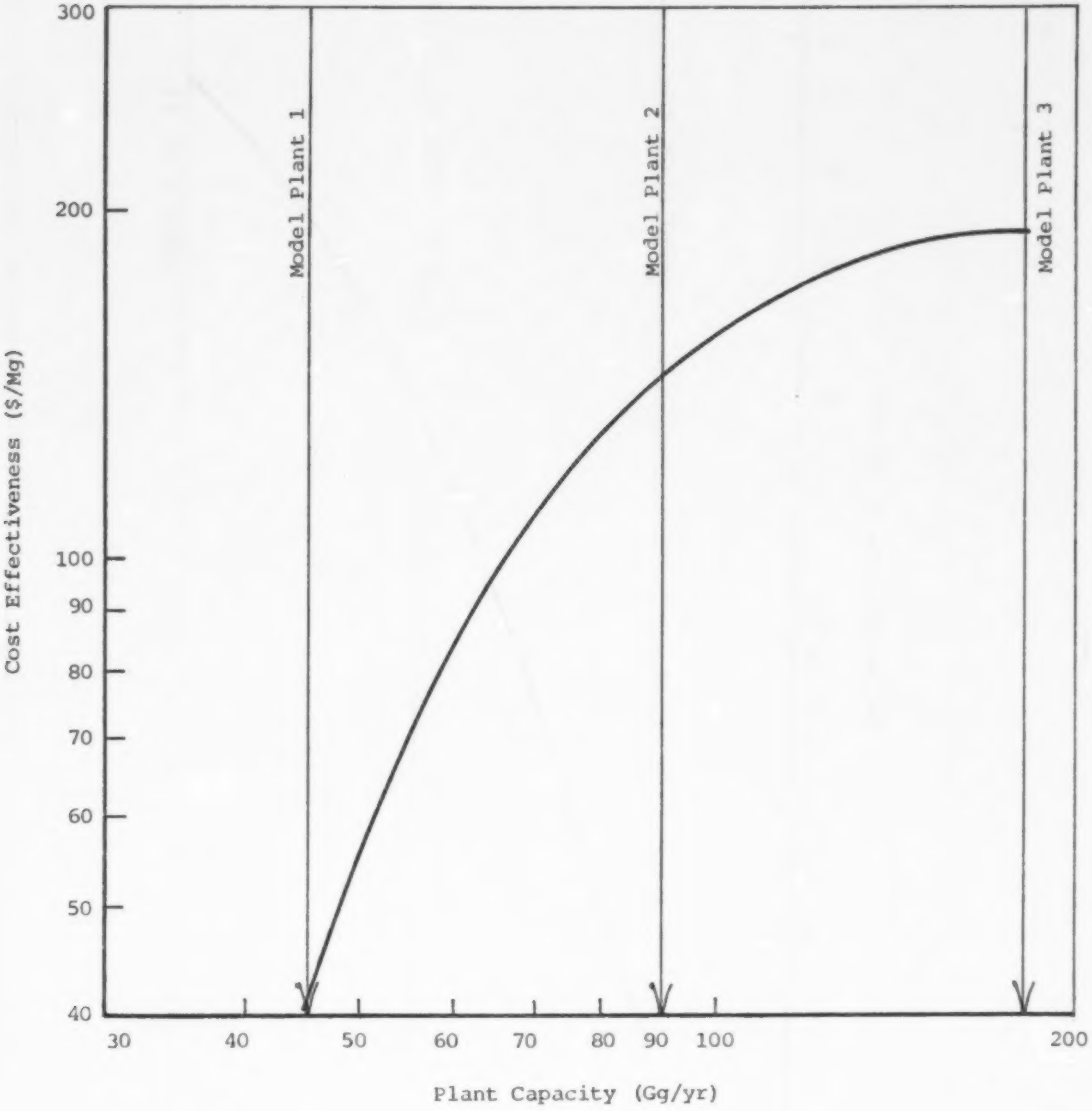

Fig. VI-3. Cost Effectiveness vs Plant Capacity for Inert-Gas Purge Vent Emission Control

Other process emissions from the methylene chloride and chloroform condensers (Vents B and C, Fig. III-1) remain uncontrolled.

2. Storage

Model-plant storage emissions can be controlled by use of condensation as described in a separate EPA report.

3. Handling Sources

No control system has been defined for the emissions from handling sources in the model plants.

4. Fugitive Sources

A control system for fugitive sources is defined in Appendix C. Fugitive emissions and their applicable controls are covered in a separate EPA report.

5. Secondary Sources

No control system has been defined for secondary emissons from the model plants.

B. ENVIRONMENTAL AND ENERGY IMPACTS

Table VI-3 shows the environmental impact of reducing VOC emissions by application of the described control systems to the model plants using the methanol hydrochlorination and methyl chloride chlorination processes. Individual impacts are discussed below.

1. Inert-Gas Purge Vent

The absorber for the inert-gas purge vent reduces net VOC emissions by 68, 136, and 272 Mg/yr for the 45,000-, 90,000-, and 180,000-Mg/yr total capacity model plants, respectively. The net VOC reduction is the reduction in methyl chloride emissions minus chloroform emissions from the absorber. The emission reduction would be equivalent to a reduction of 629 Mg of VOC for all projected domestic 1979 production of methyl chloride, methylene chloride, and chloroform by producers using the combined methanol hydrochlorination and methyl chloride chlorination process. This reduction is based on the assumption of the emission characteristics of the composite industry being equivalent to that of the model plants. A small negative environmental impact would result from the losses of chloroform from the absorber (9.6×10^{-3} kg of chloroform emissions per kg of methyl chloride recovered).

Table VI-3. Environmental Impact of VOC Emissions Control for Methanol Hydrochlorination and Methyl Chloride Chlorination Plants with Capacities of 45,000, 90,000, and 180,000 Mg/yr

Emission Source	Stream Designation (Fig. III-1)	Control Device or Technique	Emission Reductions					
			45,000-Mg/yr Plant		90,000-Mg/yr Plant		180,000-Mg/yr Plant	
			(Mg/yr)	(%)	(Mg/yr)	(%)	(Mg/yr)	(%)
Inert-gas purge vent	A	Absorber	68.0	98.8	136.0	98.8	272.0	98.8
Methyl chloride condenser	B	None						
Chloroform condenser	C	None						
In-process storage	D	Condenser	58.0	80.0	113.0	80.0	223.0	80.0
Feed and product storage	D							
By-product storage[a]	D	None						
Handling	D	None						
Fugitive	F	Detection and correction of leaks	88.1	67.5	88.1	67.5	88.1	67.5
Secondary	K	None						
Total[b]			223.5	88.2	388.6	88.0	717.1	88.0

[a] Carbon tetrachloride plus "heavies."

[b] The total percentage of emission reduction is calculated from the total uncontrolled emission listed in Table IV-1 and the total controlled emission listed in Table V-1.

2. Other Emissions (Storage and Handling, Fugitive, and Secondary)

Control methods described for these sources are condensation for in-process and final-product storage tank vents and leak correction for fugitive emissions. Application of these controls results in VOC reduction of about 146, 201, and 311 Mg/yr for the 45,000-, 90,000-, and 180,000-Mg/yr total capacity model plants, respectively. The emission reduction would be equivalent to about 929 Mg/yr for the producers using the combined methanol hydrochlorination and methyl chloride chlorination process, based on the assumption that the composite industry emissions are equivalent to the 90,000-Mg/yr model plant emissions.

VII. PRODUCT ASSESSMENT

A. SUMMARY

Three of the chloromethanes -- methyl chloride, methylene chloride, and chloroform -- are produced by the combined processes of methanol hydrochlorination and methyl chloride chlorination. Methanol hydrochlorination produces methyl chloride, which is chlorinated to methylene chloride, chloroform, and by-product carbon tetrachloride. The by-product carbon tetrachloride generally is not purified directly into product by industry.

The chloromethanes produced by the methanol hydrochlorination and methyl chloride chlorination processes are showing broad variations in consumption patterns. As is shown in Sect. II, methyl chloride consumption is expected to increase at an annual rate of about 5%, methylene chloride consumption at 11%, and chloroform consumption 8%.

Emission sources and control levels for methanol hydrochlorination and methyl chloride chlorination model plants are summarized in Table VII-1. Emission projections for domestic industry in 1979 are based on the following assumptions: (1) 50% of the methyl chloride, 70% of the methylene chloride, and 75% of the chloroform produced in 1979 were based on these combined processes, and (2) emission rates for the industry were equivalent to those for the 90,000-Mg/yr total-capacity model plant. Calculations based on these assumptions indicate VOC emissions of 236 kg/hr, with all plants uncontrolled, and 60 kg/hr, with the plants controlled. It is estimated that about 36% of the VOC emissions for the domestic methanol hydrochlorination and methyl chloride chlorination industry are controlled. This is a weighted average of the individual estimated projections:

	VOC Controlled (%)
Handling, fugitive, and secondary	20
In-process and by-product storage	10
Feed and product storage	60
Process	70

On this basis the current emissions from the domestic chloromethanes industry using the combined methanol hydrochlorination and methyl chloride chlorination processes are about 172 kg/hr.

VII. PRODUCT ASSESSMENT

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Handling, fugitive, and secondary	20
In-process and by-product storage	10
Feed and product storage	60
Process	70

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Table VII-1. Summary of Emissions from Model Plants Producing Chloromethanes by Methanol Hydrochlorination and Methyl Chloride Chlorination

Emission Source	Emission Rates (kg/hr)					
	45,000-Mg/yr Model Plant		90,000-Mg/yr Model Plant		180,000-Mg/yr Model Plant	
	Uncontrolled	Controlled	Uncontrolled	Controlled	Uncontrolled	Controlled
Inert-gas purge vent	7.85	0.10	15.7	0.20	31.4	0.40
Methylene chloride condenser	0.10	0.10	0.20	0.20	0.39	0.39
Chloroform condenser	0.029	0.029	0.058	0.058	0.12	0.12
In-process storage	2.80	1.66	5.56	3.22	10.83	6.35
Feed and product storage	5.48		10.55		20.92	
By-product storage*	0.14	0.20	0.31	0.49	0.59	0.86
Handling	1.84	1.84	3.68	3.68	7.36	7.36
Fugitive	14.9	4.84	14.9	4.84	14.9	4.84
Secondary	0.10	0.10	0.21	0.21	0.41	0.41
Total	33.2	8.87	51.1	12.9	86.9	20.7

[a] Carbon tetrachloride plus "heavies".

In addition to the emissions listed above one producer predominantly using tail-gas chlorine from a chlorine-caustic plant to feed the chlorination reactor reported process emissions averaging about 80 kg/hr.[1,2]

The predominant emission points are the inert-gas purge-vent and storage tanks. The inert-gas purge vent can be controlled by use of a chilled chloroform absorber system which if operated at -40°C would result in a net VOC reduction of 98.8%. Storage emissions can be controlled by condensation.

B. REFERENCES*

1. J. V. Muthig, Allied Chemical, Moundsville, WV, letter to D. R. Goodwin, EPA, Mar. 31, 1978.

2. Personal communcations between F. D. Hobbs, IT Enviroscience, Inc., and D. Denoon, Allied Chemical, Moundsville, WV, Sept. 14, 1978.

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*A reference located at the end of a paragraph usually refers to the entire paragraph. If another reference relates to certain portions of the paragraph, the reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.

APPENDIX A

Table A-1. Physical Properties of Chloromethane Compounds

Chemical Name	Synonym	Molecular Formula	Molecular Weight	Physical Properties						
				Physical State	Vapor Pressure	Vapor Specific Gravity	Boiling Point	Melting Point	Density	Solubility in Water
Chloromethane[a]	Methyl chloride	CH_3Cl	50.49	Gas	5.0 atm at 22°C[b]	1.78	-24.2°C at 760 mm Hg	-97.73°C	0.9159 g/ml at 20°C/4°C	4.9 g/liter
Dichloromethane[c]	Methylene chloride methylene dichloride	CH_2Cl_2	84.93	Liquid	435.8 mm Hg at 25°C	2.93	40°C at 760 mm Hg	-95.1°C	1.3266 g/ml 15 20°C/4°C	Slight
Chloroform[d]	Trichloromethane, methenyl chloride	$CHCl_3$	119.39	Liquid	200 mm Hg at 25.9°C	4.12	61.26°C	-63.5°C	1.49845 g/ml at 15°C	8.0 g/liter
Carbon tetrachloride[e]	Tetrachloromethane, perchloromethane, methane tetrachloride	CCl_4	153.82	Liquid	115.2 mm Hg at 25°C	5.32	76.54°C at 760 mm Hg	-22.99°C	1.5490 g/ml at 20°C/4°C	Insoluble

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[a] "Methyl Chloride," p. AIII-174 in Scoring of Organic Air Pollutants. Chemistry, Production and Toxicity of Selected Synthetic Organic Chemicals (f-n), edited by J. Dorigan et al., MTR-7248, Rev. 1, Appendix III, MITRE Corp. (September 1976).

[b] P. E. Liley et al., "Physical and Chemical Data," Sect. 3, Table 3-9, in Chemical Engineers' Handbook, 4th ed., edited by R. H. Perry et al., McGraw-Hill, New York, 1963.

[c] "Methylene Chloride," ibid., p. AIII-186.

[d] "Chloroform," ibid., Appendix I, p. AI-264.

[e] "Carbon Tetrachloride," ibid., p. AI-222.

APPENDIX B

Table B-1. Air-Dispersion Parameters for 90,000 Mg/yr Model Plant Using Methanol Hydrochlorination and Methyl Chloride Chlorination Processes

		Air-Dispersion Parameters				
Emission Source[a]	Emission Rate (g/sec)	Height (m)	Diameter (m)	Discharge Temp. (K)	Flow Rate (m^3/sec)	Discharge Velocity (m/sec)
Uncontrolled						
Inert-gas purge vent	4.36	11.0	0.025	253	1.55×10^{-3}[b]	1.5
Methylene chloride distillation vent	0.056	11.0	0.025	316	9.92×10^{-6}[c]	0.020
Chloroform distillation vent	0.016	11.0	0.025	316	3.64×10^{-6}[d]	0.0074
Methanol feed storage	0.29	14.63	12.80	293		
Crude product storage	0.23	7.32	5.73	308		
Methylene chloride day storage (2)	0.42	4.38	4.57	303		
Crude chloroform storage	0.07	4.88	4.45	313		
Chloroform day storage (2)	0.21	2.44	4.45	313		
Methylene chloride product storage	2.02	14.63	12.80	293		
Chloroform product storage	0.62	9.76	9.94	293		
Carbon tetrachloride storage	0.14	2.44	4.45	313		
Handling	1.02			Ambient		
Fugitive[e]	4.14			Ambient to 623		
Secondary	0.058			Ambient		
Controlled						
Inert-gas purge vent absorber	0.056	11.0	0.025	233	1.10×10^{-3}[f]	3.6
Methylene chloride distillation vent	0.056	11.0	0.025	316	9.92×10^{-6}[c]	0.020
Chloroform distillation vent	0.016	11.0	0.025	316	1.64×10^{-6}[d]	0.0074
In-process and product storage	0.89	14.6	0.025	293		
Carbon tetrachloride storage	0.14	2.44	4.45	313		
Handling	1.02			Ambient		
Fugitive	1.34			Ambient to 623		
Secondary	0.058			Ambient		

[a] One except where noted otherwise. [b] At process conditions of 5.07×10^5 Pa immediately prior to venting. [c] At process conditions of 2.07×10^5 Pa immediately prior to venting. [d] At process conditions of 1.17×10^5 Pa immediately prior to venting. [e] Fugitive emissions are evenly distributed over a rectangular area of about 40 X 80 m. [f] At process conditions of 5.07×10^5 Pa immediately prior to venting.

APPENDIX C

SAMPLE CALCULATIONS

Inert-gas purge-vent emissions were calculated for the methanol hydrochlorination and methyl chloride chlorination processes from the information given in Tables C-1, C-2, and C-3.

Table C-1. Stoichiometry and Assumed Product Yield for Determining Chlorine Requirements for Model Plants

Product	Stoichiometry	Weight Fraction of Total Capacity	Calculation	Cl_2 Product Ratio (kg/Mg)
Methyl chloride	$CH_3OH + HCl \longrightarrow CH_3Cl + H_2O$	0.25		
Methylene chloride	$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + Cl$ (70.91)* (84.93)	0.48	$\frac{70.91 \text{ X } 0.48 \text{ X } 1000}{84.93}$	400
Chloroform	$CH_3Cl + 2Cl_2 \longrightarrow CHCl_3 + 2HCl$ (70.91) (119.39)	0.25	$\frac{70.91 \text{ X } 2 \text{ X } 0.25 \text{ X } 1000}{119.39}$	297
Carbon tetrachloride	$CH_3Cl + 3Cl_2$ —— $CCl_4 + 3HCl$ (70.91) (153.82)	0.02	$\frac{70.91 \text{ X } 3 \text{ X } 0.02 \text{ X } 1000}{153.82}$	28 725

*Numbers in parentheses are molecular weights.

Table C-2. Ratios of Inert Gases in Chlorine to Total Chloromethanes Produced in Model Plants

Assumptions	Calculations	Ratios (kg/Mg)[a]	Ratios (kg moles/Mg)[b]
99.6 wt % chlorine purity, 0.4 wt % inert gases; molecular weight of inert gases, 29	$\frac{725 \times 0.004}{0.996}$	2.9	
	$\frac{2.9}{29}$		0.1

[a] kg of inert gases per Mg of product.

[b] kg moles of inert gases per Mg of product.

Table C-3. Calculated Emissions from the Inert-Gas Purge Vents in the Model Plants

Assumptions	Mole Fraction of CH_3Cl	Mole Fraction of Inert Gases	CH_3Cl Emission: Product Ratio
Pressure, 3800 mm Hg; temperature - 20°C; vapor pressure of CH_3Cl at -20°C, 880 mm Hg; molecular weight of CH_3Cl, 50.49	880 mm Hg ÷ 3800 mm Hg = 0.23	1 - 0.23 = 0.77	0.1 kg moles of inert gases per Mg of product X 0.23 X 50.49 ÷ 0.77 = 1.5 kg of CH_3Cl per Mg of product

APPENDIX D

FUGITIVE-EMISSION FACTORS*

The Environmental Protection Agency recently completed an extensive testing program that resulted in updated fugitive-emission factors for petroleum refineries. Other preliminary test results suggest that fugitive emissions from sources in chemical plants are comparable to fugitive emissions from corresponding sources in petroleum refineries. Therefore the emission factors established for refineries are used in this report to estimate fugitive emissions from organic chemical manufacture. These factors are presented below.

Source	Uncontrolled Emission Factor (kg/hr)	Controlled Emission Factor[a] (kg/hr)
Pump seals		
Light-liquid service[b]	0.12	0.03
Heavy-liquid service	0.02	0.02
Pipeline valves		
Gas/vapor service	0.021	0.002
Light-liquid service	0.010	0.003
Heavy-liquid service	0.0003	0.0003
Safety/relief valves		
Gas/vapor service	0.16	0.061
Light-liquid service	0.006	0.006
Heavy-liquid service	0.009	0.009
Compressor seals	0.44	0.11
Flanges	0.00026	0.00026
Drains	0.032	0.019

[a] Based on monthly inspection of selected equipment; no inspection of heavy-liquid equipment, flanges, or light-liquid relief valves; 10,000 ppmv VOC concentration at source defines a leak; and 15 days allowed for correction of leaks.

[b] Light liquid means any liquid more volatile than kerosene.

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*Radian Corp., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA 600/2-79-044 (February 1979).

APPENDIX E

EXISTING PLANT CONSIDERATIONS

A. Information was gathered during two site visits and through responses by industry to requests for information.

Allied, Moundsville, WV

Production is based mostly on hydrochlorination of methanol and chlorination of the resulting methyl chloride to the higher chloromethanes. A small amount (about 5%) of the capacity is based on methane, which basically is used for pressure control. The chlorine used in methyl chloride chlorination is tail-gas chlorine and therefore contains considerably more inert gases than are contained in the purified chlorine assumed to be used in the model plants. Condensation is used to reduce inert-gas purge-vent emissions by about 50%.[1,2]

Diamond Shamrock, Belle, WV

Production is based on the combined methanol hydrochlorination and methyl chloride chlorination for production of the higher chloromethanes. Two separate river-water condensation systems are used for emissions control. One system is used on multiple storage tank vents and separation and purification area process vents; 12 vents are involved. The other system is used for control of emissions from two light-ends columns and emissions resulting from the use of inert gas (nitrogen) during product and raw-material loading and unloading.[3]

Dow, Plaquemine, LA

A mixture of chloromethanes is produced by continuous hydrochlorination of methanol and chlorination of methyl chloride in a single train. Caustic scrubbing is used to control effluent losses of hydrogen chloride and chlorine. Fugitive emissions are controlled by continuous gas chromatographic monitoring of air samples collected at numerous points throughout the facility. Refrigerated condensers were reported to be planned for installation on methanol, methylene chloride, and chloroform storage tanks.[4]

Ethyl, Baton Rough, LA

Methyl chloride is produced from hydrochlorination of methanol. A flare serves the entire process, primarily for control of emergency releases from process safety valves.[5]

General Electric, Waterford, NY

Methyl chloride is produced by hydrochlorination of methanol. A condenser is used to control intermittent emissions (occurring about 75 hr each year).[6]

Union Carbide, South Charleston, WV

Methyl chloride is produced from hydrochlorination of methanol with no controls except for those necessary for good engineering operation.[7]

Vulcan, Geismar, LA

Methanol is hydrochlorinated to methyl chloride, and all methyl chloride is chlorinated to produce the higher chloromethanes. There are no process emission control devices. A refrigerated vent condenser is used for control of methylene chloride product storage emissions and is planned for control of chloroform storage emissions.[8]

Retrofitting Controls

The primary difficulty associated with retrofitting may be in finding space to fit the control device into the existing plant layout. Because of costs associated with this difficulty it may be appreciably more expensive to retrofit emission control systems in existing plants than to install a control system during construction of a new plant.

The absorption unit conceptualized for control of inert-gas purge vent emissions could be especially difficult to retrofit. It should be considered only in plants producing the higher chloromethanes because chloroform is proposed as the absorbent. Chloroform distillation capacity should also be considered at existing facilities prior to contemplation of this control device.

B. REFERENCES*

1. J. V. Muthig, Allied Chemical, Moundsville, WV, letter to D. R. Goodwin, EPA, Mar. 31, 1978.

2. Personal Communication between C. McCartel, Allied Chemical, and F. D. Hobbs, IT Enviroscience, Aug. 4, 1978.

3. S. G. Lant, Diamond Shamrock, Belle, WV, letter to D. R. Goodwin, EPA, Apr. 3, 1978.

4. F. D. Hobbs, IT Enviroscience, Trip Report for Dow Chemical Company, Plaquemine, LA, November 17, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

5. W. C. Strader, Ethyl Corporation, Baton Rough, LA, letter to D. R. Goodwin, EPA, Aug. 2, 1978.

6. R. L. Hatch, General Electric Company, Waterford, NY, letter to D. R. Goodwin, EPA, Aug. 8, 1978.

7. F. D. Bess, Union Carbide, South Charleston, WV, letter to L. B. Evans, EPA, Aug. 3, 1978.

8. F. D. Hobbs, IT Enviroscience, Trip Report for Vulcan Materials Company, Geismar, LA, Jan. 4, 1978 (on file at EPA, ESED, Research Triangle Park, NC).

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*Usually, when a reference is located at the end of a paragraph, it refers to the entire paragraph. If another reference relates to certain portions of that paragraph, that reference number is indicated on the material involved. When the reference appears on a heading, it refers to all the text covered by that heading.